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NUCLEAR OXIDATION IN THE FLAVONES AND RELATED COMPOUNDS

Part XIII. A Discussion of the Results

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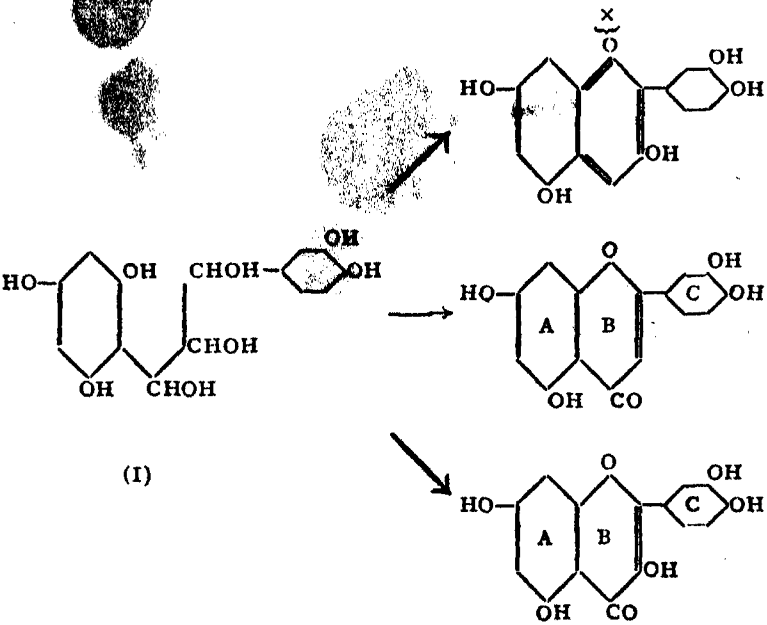
Received April 29, 1948

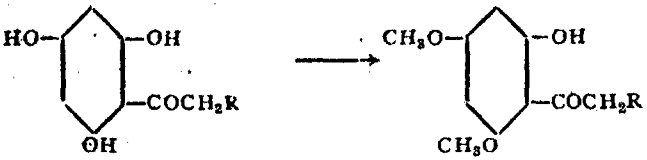
I. BIOGENESIS

In a paper by Rao and Seshadri[1] published in 1943 data bearing on the occurrence of anthoxanthins and their association in nature were presented and discussed. They were found to support the theory of Robinson regarding the origin of anthocyanins and anthoxanthins from a common precursor (I). The most outstanding structural feature of the anthoxanthins is the large number of states of oxidation in which ring (A) is capable of existing. The biological data could satisfactorily be explained on the basis that flavones and flavonols having two hydroxyl groups (5: 7) in ring (A) represent primary stages in biogenesis and those having three hydroxyls (5: 6: 7 or 5: 7 : 8) and four hydroxyls (5: 6: 7: 8) involve additional stages of oxidation.



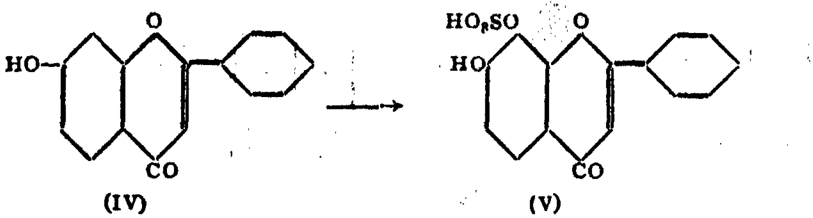
(I)

Laboratory experiments on nuclear oxidation in support of the above conclusions could not be carried out at that time owing to severe war conditions. They could be taken up more recently and the subject examined in detail. At the beginning it appeared that direct attack on the flavones themselves was not likely to be successful in view of the failures recorded in the past.[6, 7] Consequently as the first stage in the development of the model experiments phloroglucinol derivatives were chosen. Phloroacetophenone and ω-methoxy-phloroacetophenone (II) and their derivatives had not been subjected to nuclear oxidation before. In order to prevent general oxidation of the molecules the 4: 6-dimethyl ethers (III) were prepared leaving the hydroxyl in the 2-position alone free. The partial methylation is easily effected since this particular hydroxyl is definitely more resistant to methylation than the others.



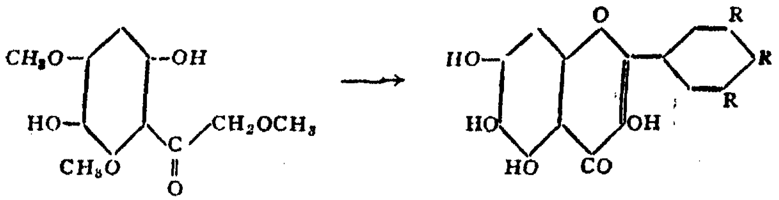
(II) R = H or OCH_3 (III)

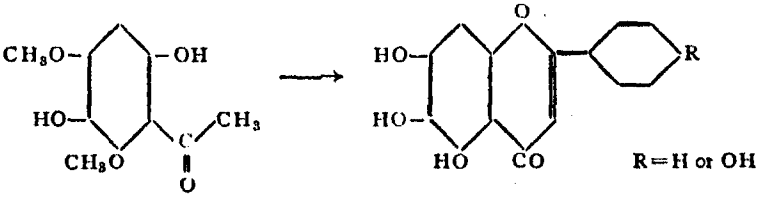
As the most suitable and direct oxidising agent alkaline potassium persulphate was chosen. It behaves as a kationoid (electrophilic) reagent and introduces a hydroxyl group in the position para to the activating group; ortho substitution is also possible as a second alternative though not so readily, if a para position is not available. As a convenient intermediate stage a sulphate ester is formed and this being soluble in water, separation of the unchanged original substance becomes easy. Subsequent hydrolysis of the ester yields the final product. In the course of our work on nuclear oxidation this intermediate sulphate could be isolated in one case[3] as a crystalline solid and characterised.



(IV) (V)

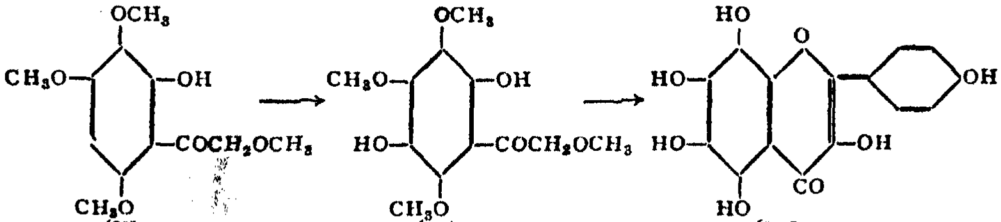
The oxidation products (VIII, VI) of phloroacetophenone and its ω-methoxy-derivative could then be subjected to the flavone condensation; thus all the four flavonols (VII) of the quercetagetin series[4] (1) 6-hydroxy-galangin, (2) nor-tangeretin, (3) quercetagetin and (4) 6-hydroxy myricetin were synthesised and so also the flavones (IX), baicalein and scutellarein.[5]


(VI) (VII)

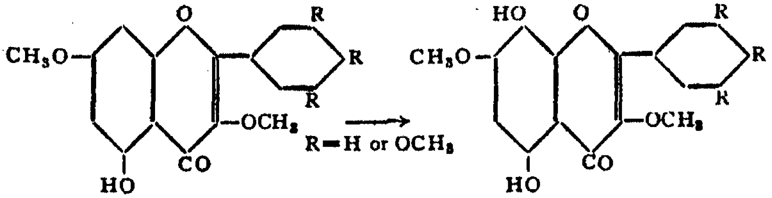


(VIII) (IX)

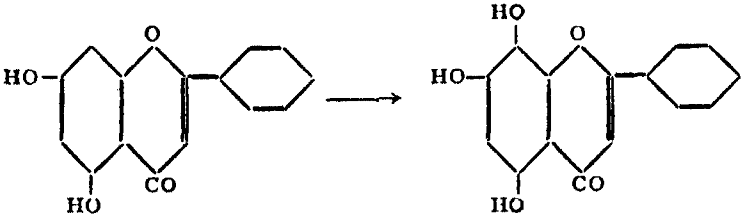
As the next higher stage, starting with gossypetol-tetramethyl-ether the flavonols of the calycopteretin series[6] could be similarly synthesised.


(X) (XI) (XII)

More recently the nuclear oxidation of typical 5:7-hydroxy flavones and flavonols could be effected. Though attempts made by earlier workers[2] had been unsuccessful the reaction was reinvestigated[7] repeatedly since the possibility of such nuclear oxidation in the flavone series was so definitely indicated by evidences from other directions. Here too partial methylation had to be first done in order to protect against general oxidation. It was found to be quite easy to carry this out leaving the resistant 5-hydroxyl alone free. Alkaline persulphate proved again to be the most satisfactory oxidising agent. At first there was difficulty owing to the very sparing solubility of these 5-hydroxy compounds in aqueous alkali. This was subsequently got over by adding the required amount of pyridine in order to get a clear solution. Thus starting from the flavonols of the quercetin series have been synthesised in an easy manner the flavonols (XIV) of the gossypetin series[7]—8-hydroxy-galangin, herbacetin, gossypetin and hibiscetin—and the flavone (XVI), nor-wogonin[8] from chrysin.



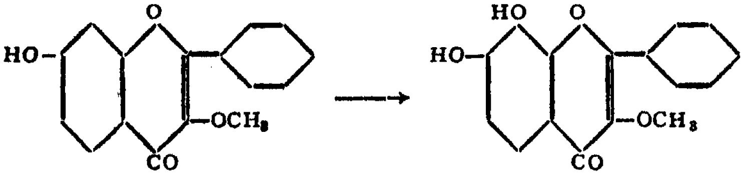
(XIII) (XIV)



(XV) (XVI)

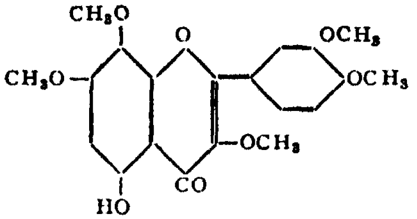
Later it was realised that it was not invariably necessary to protect the hydroxyl group in the 7-position. As a matter of fact it was an advantage to have it free in some cases since the compound was then soluble in aqueous alkali and gave rise to better yields of the oxidation product.

As shown above it is very easy to oxidise a 5: 7-hydroxy flavone into a 5: 7: 8-hydroxy compound. There seemed to be no chance of preparing the 5: 6: 7-hydroxy compounds by this means. The hydroxyl group in the 5-position activates markedly the 8-position. The simplest case is the oxidation of 5-hydroxy flavone to primetin.[9] When the 8-position is occupied as in gossypetin 3: 7: 8: 3′: 4′-pentamethyl ether[10] (XIX) no reaction takes place and the compound is recovered unchanged. As far as the hydroxyl in the 7-position is concerned it is generally known to activate position 8 in all reactions. The nuclear oxidation is no exception to this. Actually in some cases good yields of 7: 8-hydroxy compounds[8] (XVIII) could be obtained from 7-hydroxy compounds (XVII).

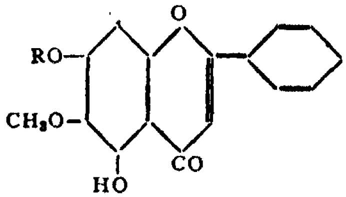


(XVII) (XVIII)

Since the free 6-position was found to be unreactive in gossypetin-pentamethyl ether (XIX), the 5: 7: 8-hydroxy flavones and flavonols cannot be used for obtaining the tetrahydroxy (5: 6: 7: 8) compounds (XII). On the other hand it is quite easy to oxidise the 5: 6-7-hydroxy compounds to the 5:6:7:8-hydroxy analogues employing the conditions already mentioned. In these cases it appeared to be necessary to protect even the 7-hydroxyl, since oroxylin-A (XX, R = H) did not give satisfactory results whereas baicalein 6:7-dimethyl ether (XX, R = CH_3) underwent the change smoothly.[11] From nortangeretin, calycopeteretin and from quercetagetin, 6:8-dihydroxy quercetin have been prepared[10] (XXI → XXII).

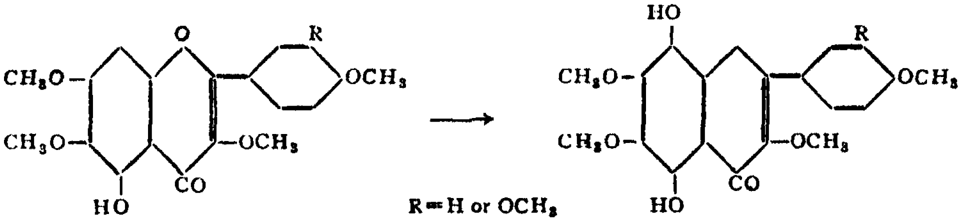


(XIX)



R = H or CH_3

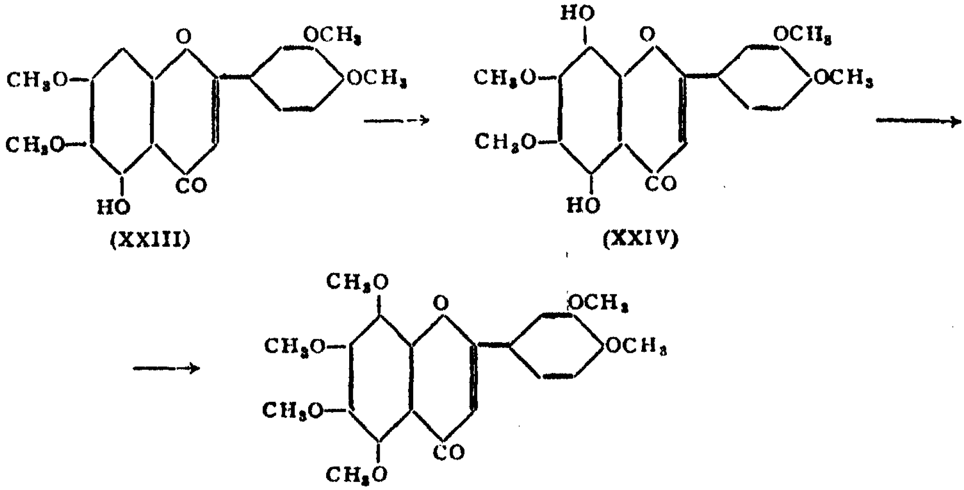
(XX)



R = H or OCH_3

(XXI)

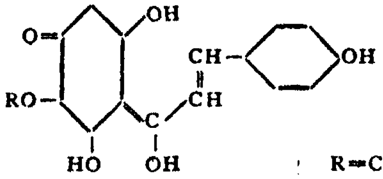
Similarly the synthesis has been carried through using the flavones, baicalein, scutellarein and 6-hydroxy-luteolin (XXIII) and members of the nobiletin (XXV) (nornobiletin) series obtained.[11, 12]



(XXIII) (XXIV)

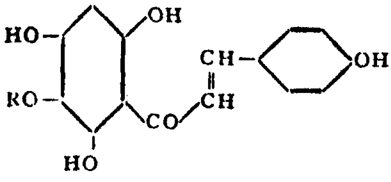
(XXV)

The experimental results described so far would lead to the following conclusions regarding the evolution in nature of compounds with three and four hydroxyl groups in ring (A). (1) 5: 7-Hydroxy-flavones and flavonols as well as their analogues with ring (B) open are involved in the oxidation. Partial protection of the hydroxyl groups is effected whatever may be the mechanism adopted. (2) 5: 7: 8-Hydroxy-flavones and flavonols (gossypetin and norwogonin series) result from the corresponding 5: 7-hydroxy-flavones and flavonols by nuclear oxidation in the 8-position. This takes place very readily in the laboratory. Though the alternative, that is, the nuclear oxidation of the open form and subsequent ring closure to yield this type could not be altogether excluded, it seems to be unlikely as will be discussed below. (3) For the formation of the 5: 6: 7-hydroxy-flavones and flavonols the oxidation should involve the open form and the ring closure should take place subsequently. It has already been mentioned that these compounds cannot be produced from the fully formed 5: 7-hydroxy-flavones themselves since the nuclear oxidation of the 6-position does not take place particularly when the 8-position is unsubstituted. As satisfactory model experiments could be taken the oxidation of phloroacetophenone and ω-methoxyphloroacetophenone-dimethyl ethers already described (III → VIII). Among compounds more closely related to flavones and with the ring (B) open, chalkones could be taken for experimentation. These occur in nature and examples with the ring (A) containing four and five hydroxyl groups (free or methylated) are found in carthamin[13] (XXVI) and *iso*-carthamin (XXVII) and pedicin, pedicellin (XXVIII) and their allies.[14, 15]

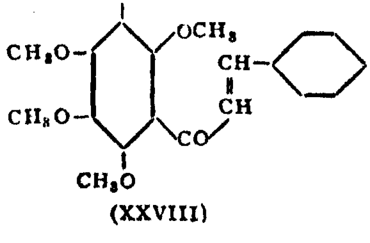


(XXVI)

$R = C_6H_{11}O_5$



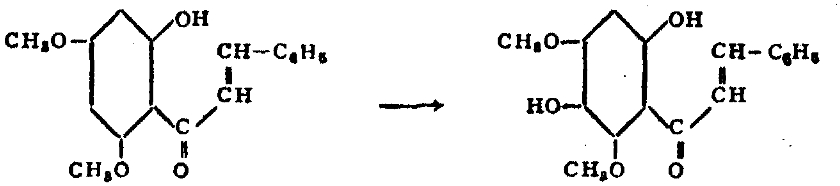
(XXVII)



(XXVIII)

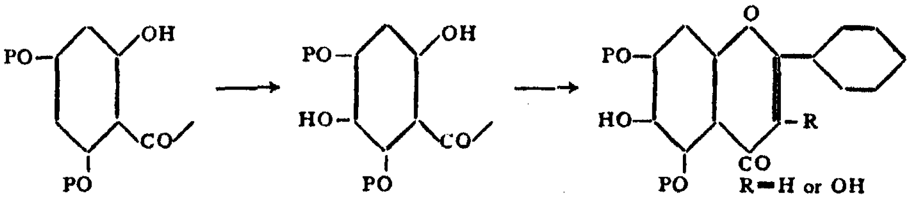
Experiments have now been carried out using 2-hydroxy-4-methoxy-chalkone and 2-hydroxy-4: 6-dimethoxy chalkone[16] (XXIX). They give rise to the

5-hydroxy compounds (XXX) under almost the same conditions as the simpler ketones.



(XXIX) (XXX)

Here it may be contended that in the plant after the oxidation of the open structure, ring closure could take place in either of two ways leading to the 5: 6: 7-hydroxy compounds or the 5: 7: 8-hydroxy compounds. The latter possibility seems to be very small from the following considerations. In laboratory experiments the 5: 6: 7-hydroxy flavones have greater stability and are formed in preference; in several cases 5: 7: 8-hydroxy flavones undergo isomeric change into the 5: 6: 7-type when boiled with hydriodic acid (see for discussion Sastri and Seshadri[6, 17]). Further, since some kind of protection of the hydroxyl groups is employed as indicated below, the ring closure to the 5: 6: 7-hydroxy form (XXXII) will be the most direct.



(XXXI) (XXXII)

P=Protecting group

(4) The 5: 6: 7: 8-hydroxy-flavones and flavonols are produced by the nuclear oxidation of the corresponding 5: 6: 7-hydroxy compounds. This has been found to take place easily in the laboratory.[10, 11, 12] The occurrence of tangeretin and nobiletin in the closely related species of citrus nobilis has been mentioned in this connection. The alternative formation from the oxidation of the appropriate open form analogous to gossypetol-tetramethyl ether[6] (X) cannot be excluded though this process may be less direct. Actually pedicin, pedicellin and its associates are the results of such complete hydroxylation in the chalkone group (see Rao and Seshadri[15]). The case of pedicin and related compounds is discussed in detail later on.

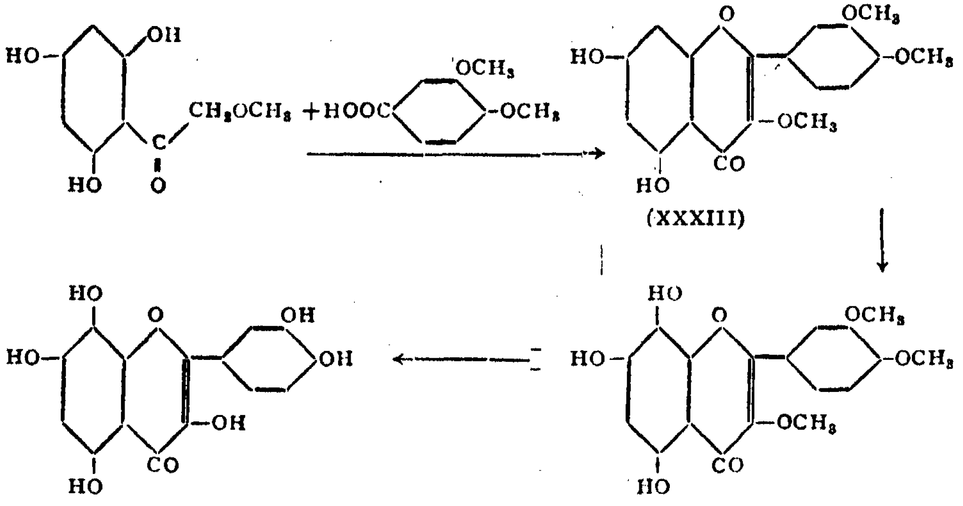
II. PARTIAL PROTECTION

The necessity for the protection of the large number of hydroxyl groups in order to escape general oxidation has now to be emphasised. This also seems to direct the course of the nuclear oxidation. In the laboratory partial methylation can be conveniently adopted. Benzyl groups can also be used for this purpose and their more easy removability renders them handy in special cases though benzyl ethers are more difficult to prepare and to oxidise. In nature too protection of hydroxyl groups should be in operation whatever may be the protective mechanism involved. Probably the simplest suggestion would be that the protection is effected by a process of absorption or chemisorption on the enzymes required for biological oxidation. Such a mechanism has been suggested by Cook[18] in connection with the hydroxylation of carcinogenic hydrocarbons in the animal body.

In the case of the flavones and flavonols the 5-hydroxyl is definitely more resistant than the others and hence is left conveniently out during partial protection. It is then free to activate the 8-position giving rise to the easy formation of the 5:7:8-hydroxy compounds. Regarding the related open forms (*e.g.*, chalkones) it is again interesting to note that only one orthohydroxyl is resistant to methylation or protection[4, 5] (see also Robertson, Robinson and Struthers[19] for explanation) and partial protection can therefore be conveniently provided leaving out this hydroxyl which can then activate the available para position. Hence the schemes given above based on partial protection of the phenolic hydroxyl groups become valid.

III. SIMPLIFICATION OF THE SYNTHESIS OF NATURALLY OCCURRING FLAVONES

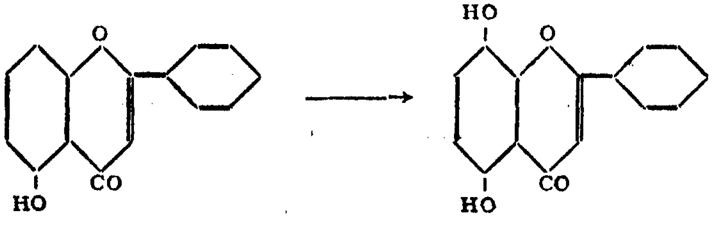
It is not infrequent that efforts to understand the methods of Nature lead to considerable simplification of laboratory methods of synthesis. The classical example of Robinson's synthesis of tropinone is well known. As a result of the experiments on nuclear oxidation a large number of naturally occurring flavones and flavonols have now been synthesised by methods which are direct and simple and mean considerable improvement over older methods. The new syntheses of the flavonols of the quercetagetin series[4] and of baicalein and scutellarein[5] have already been mentioned. These involve the oxidation of the partial methyl ethers of phloroacetophenone and ω-methoxy phloroacetophenone. Nuclear oxidation of the flavones themselves have led to more important results. Thus gossypetin, herbacetin and hibiscetin[7] are readily prepared from quercetin, kaempferol and myricetin. From the point of view of total synthesis the discovery that partial methyl ethers (XXXIII) with both 5 and 7-hydroxyl groups free, undergo oxidation more readily than the 5-hydroxy compounds is a definite advance, because these dihydroxy-compounds are the immediate products of Allan-Robinson synthesis. The following illustration takes the case of gossypetin (XXXIV) synthesised from quercetin trimethyl ether.



(XXXIII)

(XXXIV)

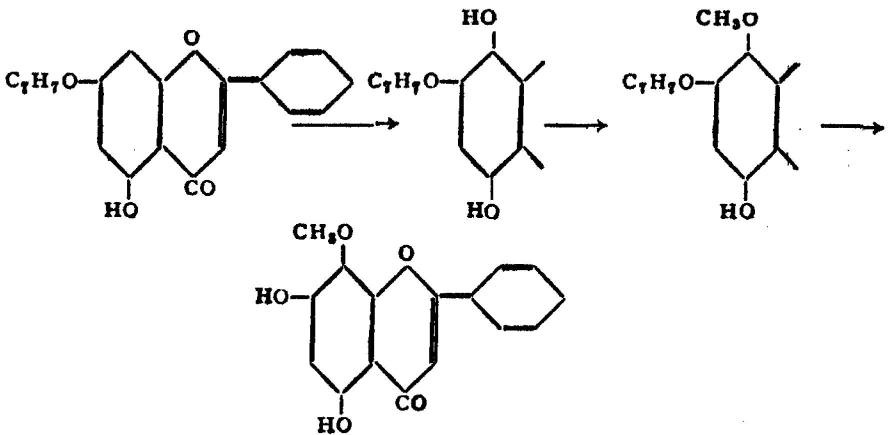
More complex examples are the synthesis of calycopteretin and its higher analogue[10] from nortangertin and quercetagetin and of nobiletin[12] and its group[11] from the flavones of the baicalein series. Norwogonin and primetin are simpler compounds, but there was originally considerable difficulty in their synthesis. Besides the usual difficulties of the preparation of flavones as compared with flavonols, such as poor yields and 3-acylation, in these cases there was the additional difficulty arising from isomeric change during demethylation. However nuclear oxidation of chrysin (XV) and 5-hydroxy flavone (XXXV) takes place smoothly and norwogonin[8] (XVI) and primetin[9] (XXXVI) can be obtained pure with great ease.



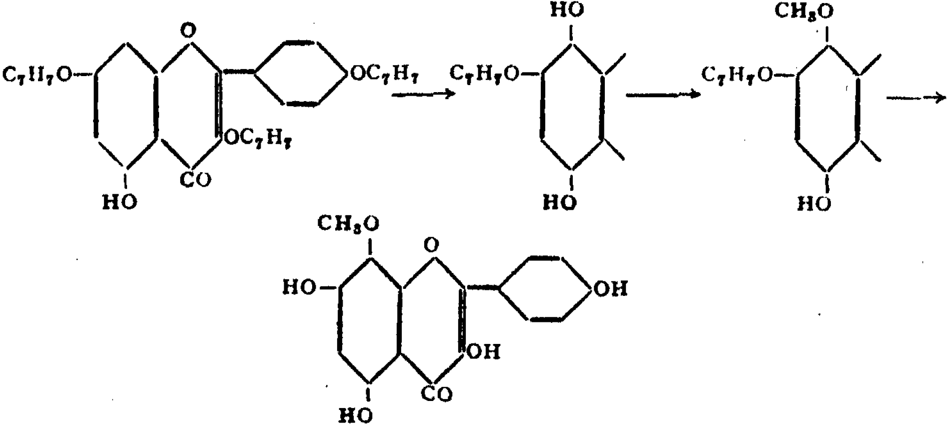
(XXXV)

(XXXVI)

Another interesting application of nuclear oxidation is in the synthesis of the partial methyl ethers, wogonin[20] (XXXVII) and tambuletin[21] (XXXVIII). These involve initial protection of some hydroxyl groups by benzylation and removal of the benzyl groups finally.

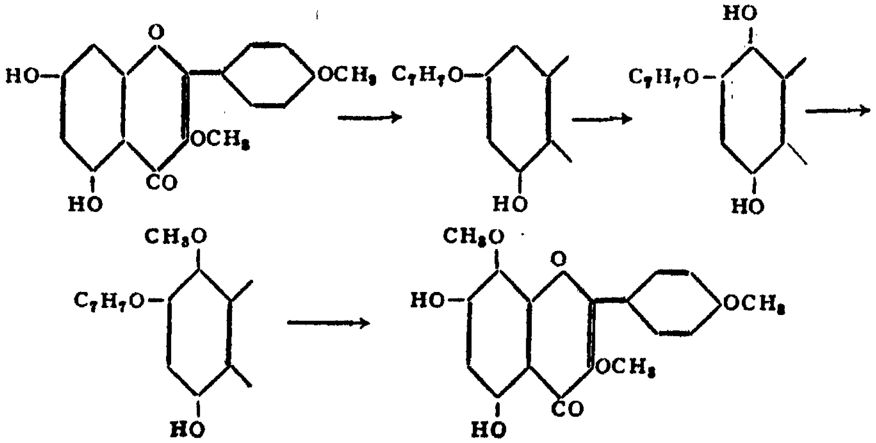


(XXXVII)



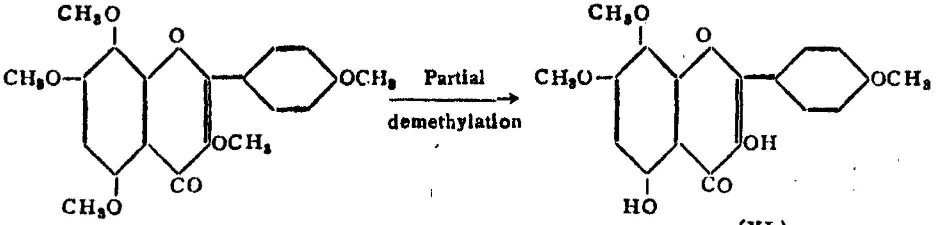
(XXXVIII)

Tambulin was originally considered to be 3:8:4′-trimethyl ether of herbacetin (XXXIX). This partial ether was prepared in the following manner.[22]



(XXXIX)

The product was however found to be different from tambulin. Examining other possibilities it has been shown that it should have the constitution of 7:8:4'-trimethyl ether of herbacetin (XL).[23] This ether is conveniently prepared by the partial demethylation of pentamethyl herbacetin using aluminium chloride.

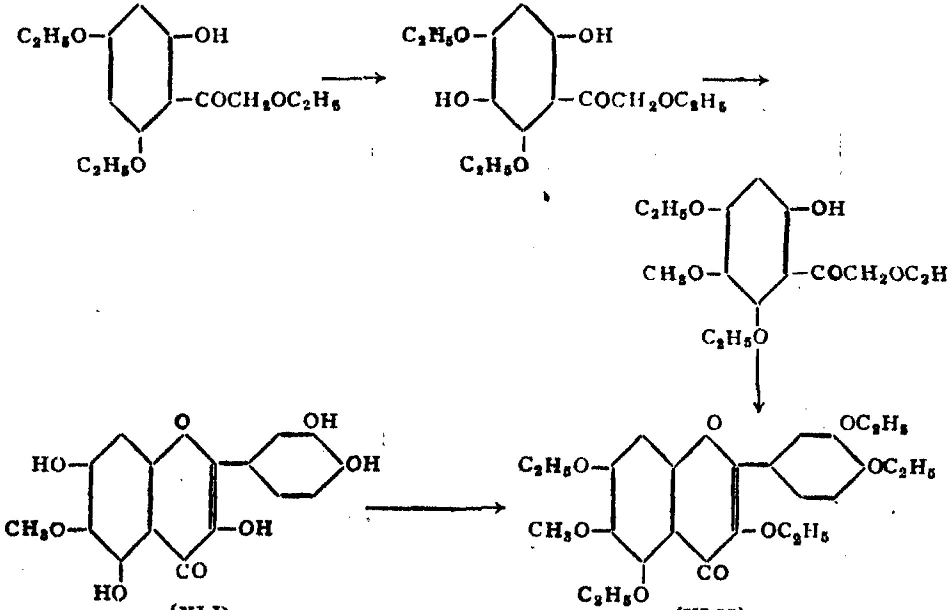


(XL)

IV. STUDY OF CHEMICAL CONSTITUTION

The method of nuclear oxidation is particularly useful in the study of the chemical constitution of glycosides and partial methyl ethers of anthoxanthins having three and four hydroxyls in ring (A). It has been successfully applied to a number of cases and has resulted in considerable simplification of the work and definiteness of the conclusions.

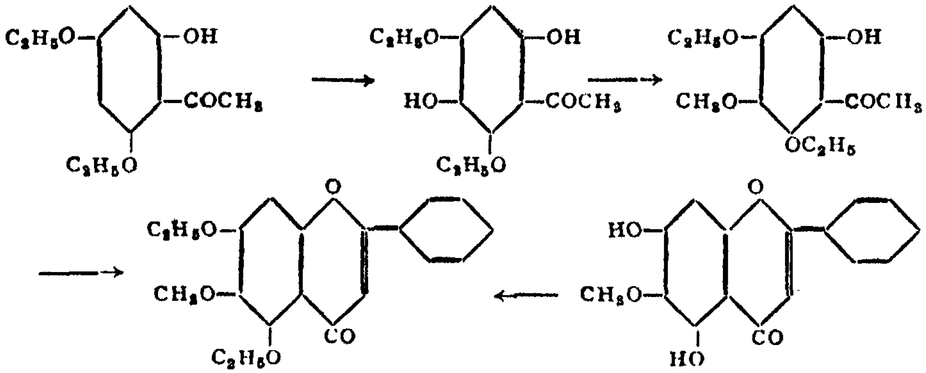
(*a*) *Partial methyl ethers.*—The earliest example was patuletin (XLI). That it is the 6-methyl ether of quercetagetin[24] was surmised from a comparison of its colour reactions with those of suitably chosen related compounds. This was then confirmed[25] by the preparation of pentaethyl patuletin (XLII) and its synthesis from ω-ethoxy phloroacetophenone. The



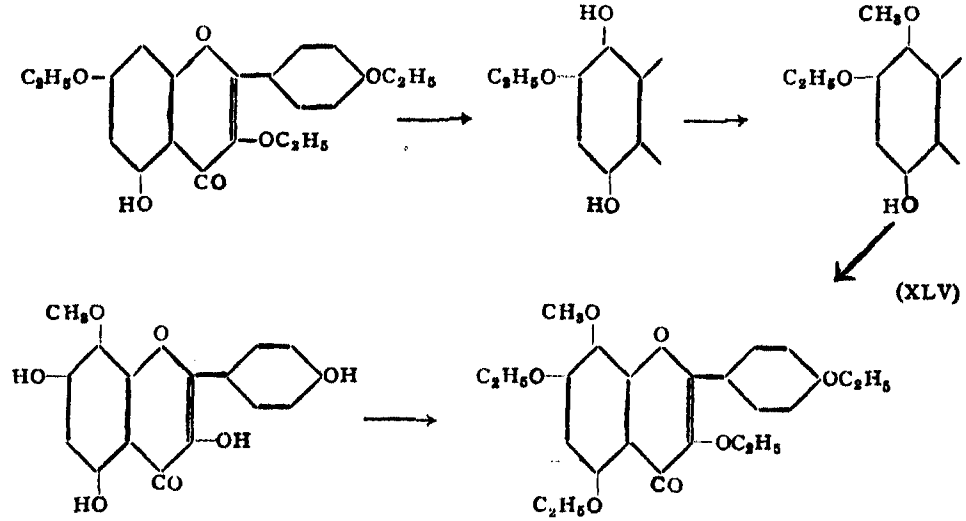
(XLI) (XLII)

use of ethylation for this purpose and the study of the mixed ethers is a marked improvement in this type of work. The presence of free hydroxyl groups in these partial ethers is a disadvantage in both degradation and synthetic work. The difficulty is removed by ethylation and hence it has been adopted regularly in this laboratory.

Oroxylin-A (XLIII)is a similar case. It is the 6-methyl ether of baicalein and its constitution was also established in an analogous manner by the synthesis of its diethyl ether starting from phloroacetophenone.[26]


(XLIII)

An example where the nuclear oxidation of a flavone itself has been employed is that of tambuletin[27] (XLIV). Its constitution as the 8-methyl-ether of herbacetin was inferred from its properties and colour reactions. This was confirmed by the preparation of its triethyl (XLV) and tetraethyl (XLVI) ethers and their synthesis[28] as follows:

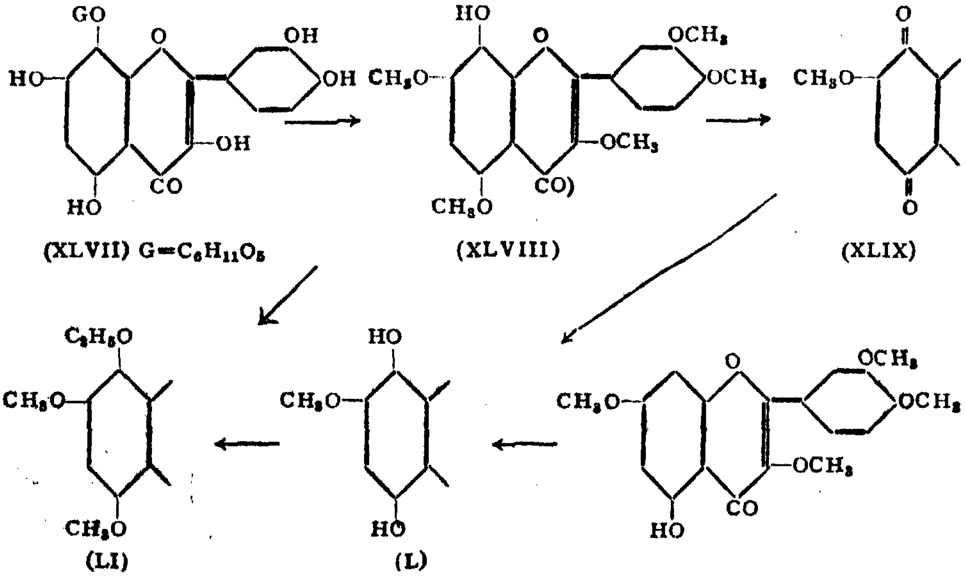

(XLV)

(XLIV)

(XLVI)

Later tambuletin itself was synthesised as already mentioned. This technique of nuclear oxidation along with ethylation has also been employed in the study of the constitution of tambulin.[32]

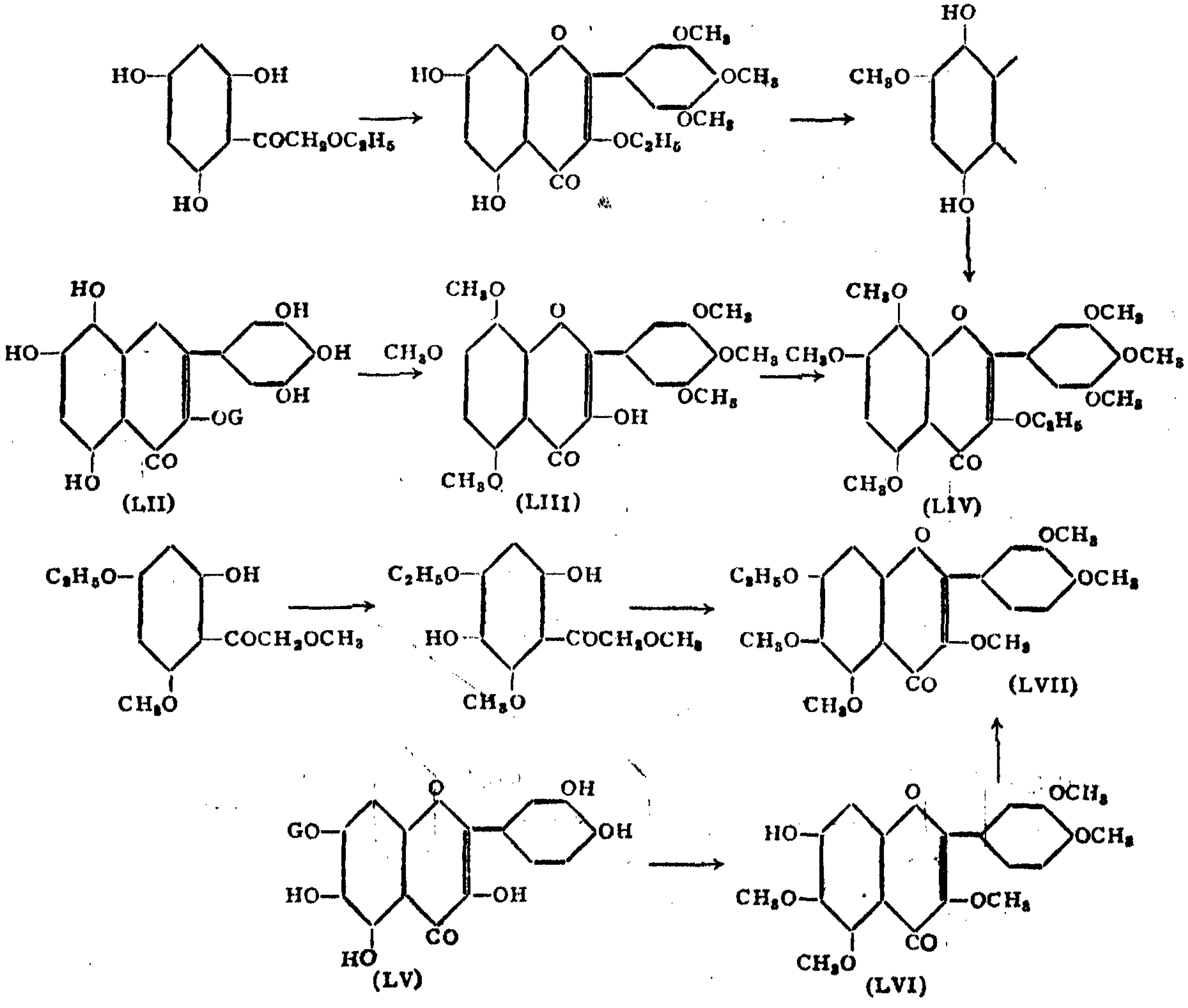
(*b*) *Anthoxanthin glycosides.*—The application of this method of nuclear oxidation to the study of glycosides can be illustrated using gossypin and hibiscitrin. The former is 8-mono-glucoside of gossypetin (XLVII) and belongs to an unusual type. This conclusion was first arrived at from a consideration of its properties and reactions.[29] When fully methylated and the product hydrolysed a partial methyl ether with only one hydroxyl left out was obtained. It did not undergo fission with alkali satisfactorily; but veratric acid could be isolated as one of the products and this indicated that the free hydroxyl was in the benzopyrone part. The location of the hydroxyl in the 8-position (XLVIII) was first established by eliminating other possibilities using synthetic samples. This was supported by the oxidative demethylation[30] of this partial methyl ether yielding flavoquinone (XLIX) which could be reduced to the flavoquinol (L). This flavoquinol could be readily prepared, as already mentioned by the persulphate oxidation of tetramethyl-quercetin.[7] The conclusive stage was the ethylation of the partial methyl ether (XLVIII). The mixed ether (LI) not only underwent smooth alkali fission, but it could be easily synthesised by the stepwise ethylation and methylation of the flavoquinol (L) thus fixing the position of the ethoxyl and hence of the original glucose group unequivocally in the 8-position.



(XLVII) G=$C_6H_{11}O_5$ (XLVIII) (XLIX)

(LI) (L)

Hibiscitrin[31] is a monoglucoside of hibiscetin and belongs to a different type. On methylation and hydrolysis it yielded a hexa-methyl ether having one free hydroxyl group. Here again alkali fission yielded only the acid part as trimethyl gallic acid; the free hydroxyl was therefore in the benzopyrone half of the molecule. From a consideration of the properties of the glucoside and the degradation product the free hydroxyl was located to be in the 3-position (LIII) and hence hibiscitrin was a 3-glucoside (LII). The other alternative positions were also eliminated by the synthesis of suitable reference compounds for comparison. The method of nuclear oxidation made this work considerably easy. Final confirmation was obtained by ethylating (LIII) and synthesising the mixed ether (LIV) as follows. This compound further underwent smooth degradation with alkali to yield a ketonic part which could be definitely identified.

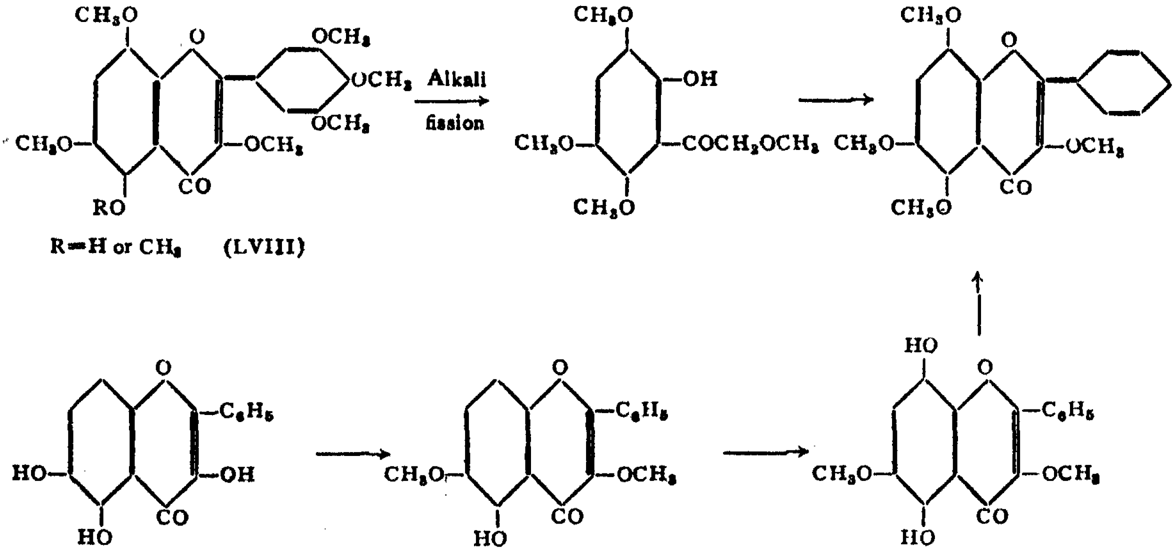


(LII) (LIII) (LIV) (LVII) (LV) (LVI)

Quercetagitrin (LV) the monoglucoside of quercetagetin, forms a third typical example. After methylation and hydrolysis it yielded a pentamethyl ether of quercetagetin. Its properties and reactions and particularly the behaviour of the allyl ether indicated that the free hydroxyl was in the 7-position (LVI).[32] This has now been conclusively established by preparing its ethyl ether (LVII) and synthesising it in the manner[33] shown in page 14.

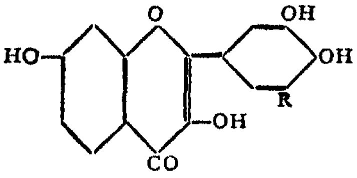
V. GARDENIN

Gardenin[34] (LVIII, R = H) is a partial methyl ether of a flavonol belonging to a novel type not known before. That it has the 5: 6: 8-arrangement of substituent groups was arrived at by the elimination of all other possibilities. Definite confirmation of this constitution has recently been provided by Balakrishna and Seshadri[35] by synthetic experiments using nuclear oxidation as indicated below:

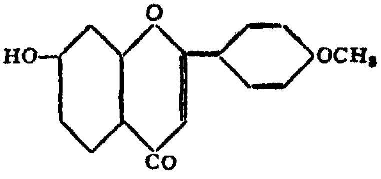


R = H or CH$_3$ (LVIII)

Flavones without the hydroxyl in the 7-position are rare in nature. Besides gardenin only primetin and 5-hydroxy flavone occur. They seem to result from the selective removal (reduction) of this hydroxyl at some stage of evolution. On the other hand fisetin (LIX, R = H) and robinetin (LIX, R = OH) are two flavonols devoid of the 5-hydroxyl group and pratol is a flavone (LX) of this type; again there are indications of the occurrence of 6: 7: 8-hydroxy-flavonols in the plant kingdom. Simple flavone which occurs as dust on various species of primula is an extreme case and lacks both these hydroxyl groups.



(LIX)

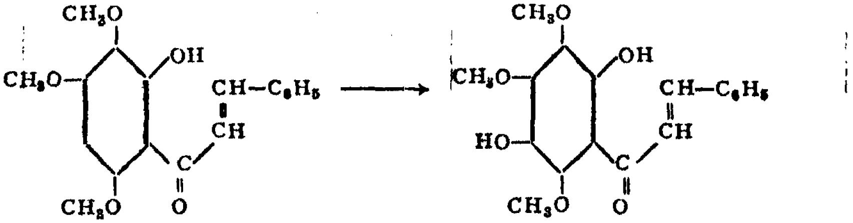


(LX)

VI. PEDICIN AND ITS DERIVATIVES

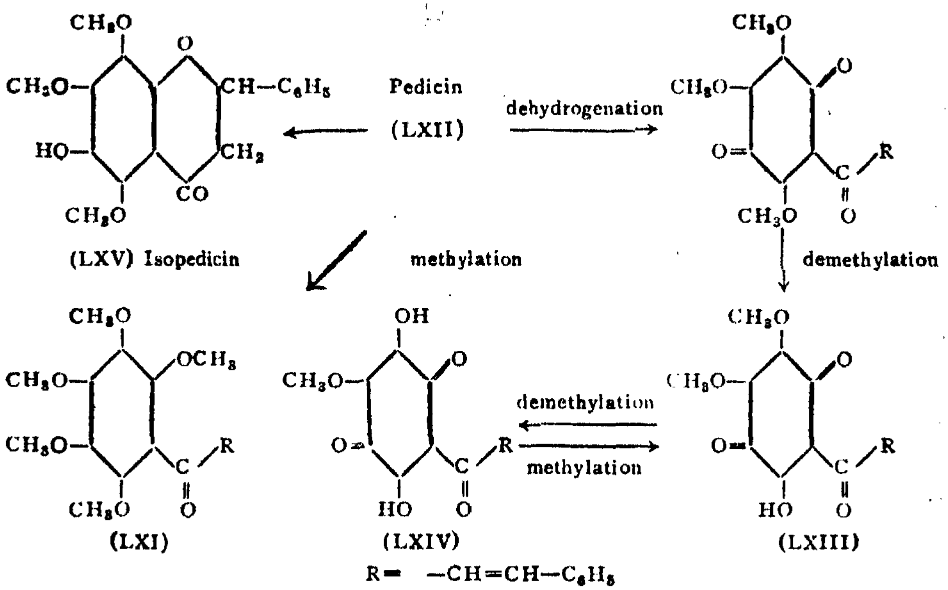
Mention has already been made that pedicin, pedicellin and their allies are examples of chalkones in which ring (A) is completely substituted. An interesting application has been made of nuclear oxidation in the recent study of this group of compounds. It is based on the easy formation by this method of *p*-dihydroxy chalkones which are otherwise not easily accessible.

The main crystalline components isolated by Siddiqui[36] from the leaves of Didymocarpus pedicellata are (1) pedicin, (2) isopedicin, (3) pedicellin and (4) pedicinin. The constitution of pedicellin was readily established as the fully methoxylated chalkone (LXI)[14] and its synthesis carried out by Baker.[37] There was some difficulty regarding the structure of pedicinin because that of pedicin was not correctly given; Sharma and Siddiqui[14] considered the latter to be an ortho-dihydroxy compound. From biogenetic considerations and from its reactions it appeared to us that this required revision and that pedicin should be a paradihydroxy compound (LXII). It has been shown to be so[15] and the new constitution has been confirmed by synthesis as follows:



(LXII)

The correct constitution of pedicin has thrown fresh light on the formula of pedicinin (LXIV) and on the biogenesis of the various compounds including methyl-pedicinin (LXIII) which has also been isolated from the leaves in this laboratory. Pedicin (LXII) which is a major component of the leaves, is considered to be the primary member formed according to the above synthetic process. The evolution of the others is indicated in the scheme given below and all the stages have been proved experimentally.



SUMMARY

The results contained in the recent publications from this laboratory on the subject of nuclear oxidation in the flavones and related compounds are summed up. Originally the main interest was in the theory of biogenesis of anthoxanthins; the bearing of the results on the evolution of the various types of flavones and flavonols is therefore discussed in detail. This study has led to the development of considerably simplified methods of synthesis of all the naturally occurring substances with three and four hydroxyl groups in ring A and of the special though simpler compounds like primetin. The application of this oxidation method along with ethylation for the establishment of the structure of partial methyl ethers as well as glycosides is illustrated by a number of typical examples. Special mention is made of the interesting and novel cases like gardenin and pedicin.

Note added in proof. In the above discussion of the persulphate oxidation and of the applicability of the results to the biogenesis of anthoxanthins, the benzopyrone part alone has been considered in detail. This is because the outcome of laboratory experiments regarding the side phenyl nucleus continued to be inconclusive. However, since submitting this paper for publication more definite results have been obtained and they will be published in a forthcoming paper.

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CHEMICAL INVESTIGATION OF INDIAN FRUITS

Part V. Constitution of Auranetin

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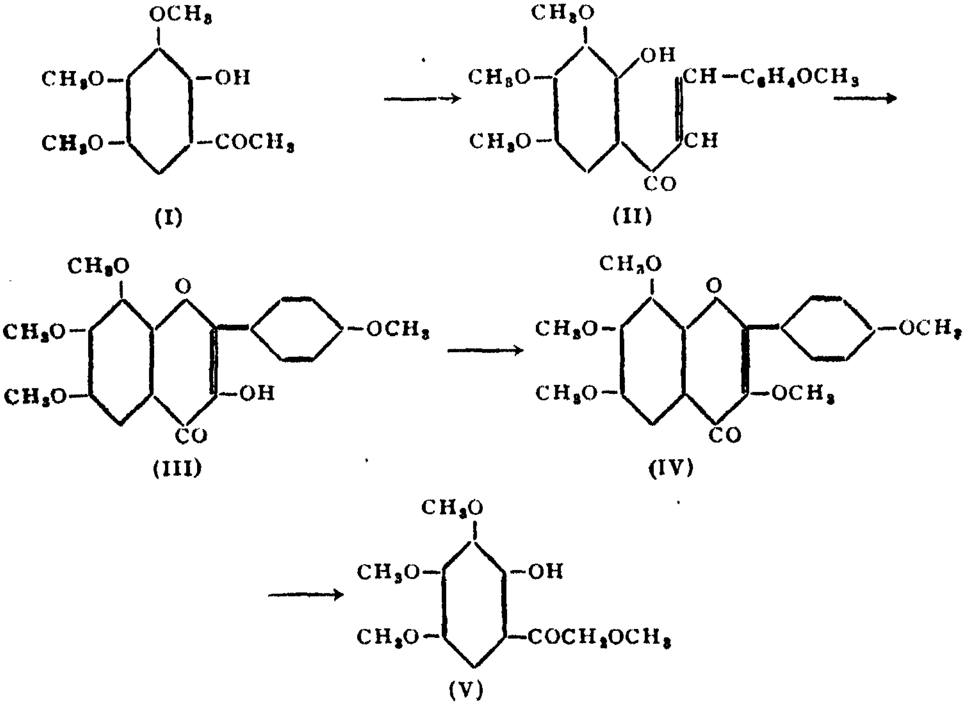
IN an earlier paper (Part III[1]) was reported the isolation of a new compound in a small yield from the loose peels of kamala oranges, a local variety of *Citrus aurantium*. It was a fully methylated flavone like tangeretin and nobiletin and appeared to be a new entity found in the Citrus. It was named 'aurantin' based on its natural occurrence but it was realised later that this name had already been given to another substance isolated from the fungus *Oospora aurantia* (Cooke).[2] The name of the citrus product is now therefore changed to 'auranetin'.

The progress of work on the constitution of auranetin has been rather slow since, besides the difficulties of war years, the yield of the compound was very low and its purification was difficult. We examined similar fruits from other localities with the object of discovering a better source. So far this has been unsuccessful. The fruits from other places have not yielded any auranetin. Consequently a good portion of the earlier work had to depend on comparison with other known compounds.

The original sample of auranetin was not pure though it was crystalline. As the result of further work it has been possible to get colourless samples with a considerably higher melting point (139–40°). Its molecular formula is now definitely established as $C_{20}H_{20}O_7$ and it contains five methoxyl groups. Fission with alcoholic potash yielded anisic acid and a pale yellow ketone melting at 116–17° and having the formula $C_{12}H_{16}O_6$ with four methoxyl groups. It could not be studied further owing to lack of material. However the isolation of anisic acid narrowed down the possibilities. Auranetin was definitely different from tangeretin and pentamethyl herbacetin and the mixed melting points were lowered. The lower member of the nobiletin series (5 : 6 : 7 : 8 : 4′-pentamethoxy flavone) was then prepared.[3] It was found to melt at 150-51°. It was therefore clear that auranetin was a flavonol ether and the fairly smooth fission of the compound with alkali supported this opinion. Of the four possible structures for the flavonol pentamethyl ether, two, tangeretin and pentamethyl-herbacetin, were already ruled out. The other two would have the 5: 6: 8 and 6: 7: 8 arrangement of methoxyl groups. The former though uncommon had recently been found in gardenin and 3: 5: 6: 8: 4'-pentamethoxy flavone[4] was therefore prepared for comparison. Its melting point was 142–43° which was very nearly that of auranetin; but a mixture of the two melted markedly lower. Thus by elimination auranetin should have the constitution of 3: 6: 7: 8: 4'-pentamethoxy flavone (IV). Flavonols with the 6: 7: 8-arrangement of hydroxyl or methoxyl groups have not so far been found to occur in nature. But the compound having the above constitution has been prepared a few years back by Bargellini and Oliverio[5] synthetically using the following steps.



The recorded properties of the pentamethyl ether, penta-hydroxy flavone and its acetate agreed with those of auranetin, norauranetin and its acetate. The melting points are compared in Table I. For purposes of direct comparison the compounds were synthesised. Since the original paper of Bargellini and Oliverio was not available at that time and only the abstract could be obtained, the methods of our preparation, being somewhat different, are briefly given. The agreement between the natural and synthetic samples is complete. Further the alkali fission of the synthetic pentamethyl ether yields besides anisic acid, 2-hydroxy-ω: 3: 4: 5-tetramethoxy-acetophenone

(V) which is found to be identical with the ketone obtained from auranetin. Hence the identity of the two series, natural and synthetic, is established.

TABLE I

	Natural compounds	Synthetic compounds	
		Bargellini and Oliverio	Ours
1. Pentahydroxy compound ..	Above 360°	Above 360°	Above 360°
2. Methyl ether (Auranetin) ..	139–40°	141°	139–40°
3. Acetate ..	220–21°	216°	220–21°
4. Fission ketone ..	116–17°	..	116–17°

Thus in auranetin the citrus fruits have made another notable contribution to the chemistry of flavones. The American tangerine oranges provided the first fully methylated flavone, tangeretin[6] indicating the existence of a powerful methylation mechanism capable of attacking even the resistant 5-hydroxyl group. The Chinese mandarin oranges yielded nobiletin[7] which is not only a fully methylated flavone with six methoxyl groups, but has further a fully oxidised condensed benzene nucleus (5:6:7:8). The Indian kamala oranges have made the third contribution. Auranetin is another fully methylated compound and represents the so far unrepresented 6:7:8-combination of methoxyl groups. With this discovery the occurrence in nature of all the possible arrangements of three hydroxyl or methoxyl groups in the condensed benzene nucleus has been established. The most common are the 5:6:7 and 5:7:8 orientations and they are represented by a number of compounds. The 5:6:8-arrangement in which the 7-position is free is rare and it is represented only by the recently discovered gardenin. Similarly the 6:7:8-orientation of groups in which the 5-position is unsubstituted is equally rare and auranetin becomes the only known representative. Its evolution from the fundamental 5:7-hydroxy (quercetin) type should involve stages of oxidation of the positions 6 and 8 and reduction of the position 5 somewhat analogous to what has been suggested for gardenin.[8] In view of the considerations discussed in a recent publication[9] the following alternative seems to be the most probable.

$$5:7 \rightarrow 5:6:7 \rightarrow 5:6:7:8 \rightarrow 6:7:8$$

Though the removal of the 5-hydroxyl group may be possible at an earlier stage, oxidation of position 8 is best promoted by the presence of this group and it is therefore retained till the last stage in the above scheme.

EXPERIMENTAL

Isolation of Auranetin

The peels of the kamala oranges were sun dried and cut into small pieces and extracted with ligroin by heating on a water-bath for 10 hours; the yellow extract was poured out and the extraction repeated twice more. The extracts were combined and the solvent was distilled off under reduced pressure as competely as possible. The deep yellow oily residue was poured into an evaporating basin and the last traces of the solvent allowed to evaporate. The semi-solid product was triturated with cold methyl alcohol when most of the waxes and carotenoids remained undissolved and were filtered off. The methyl alcoholic solution was then evaporated and the remaining oily residue was dissolved in a small quantity of ether (1 volume) and diluted with four volumes of petroleum ether. A pale yellow crystalline solid began to separate in about a day; after a few days it was filtered and washed with a small quantity of petroleum ether to remove the adhering oil, and recrystallised from ether-petroleum ether mixture, when auranetin separated as almost colourless (very pale yellow) fine needles, m.p. 139–40°. (Found: in air-dried sample: C, 61·7; H, 6·0; loss on drying at 110° *in vacuo*, 4·2%; OCH_3, 40·2%; $C_{20}H_{20}O_7$, H_2O requires C, 61·5; H, 5·6; H_2O loss, 4·6%; OCH_3 for five OCH_3 groups, 39·7%. Found in the vacuum dried sample: C, 64·2; H, 5·8; OCH_3, 41·2; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4; OCH_3, 41·7%). The other properties and the reactions of auranetin were the same as described in detail in a previous paper.[1]

Nor-auranetin

Auranetin was demethylated with hydriodic acid as already described and nor-auranetin was recrystallised from a mixture of alcohol and acetic acid. It appeared as yellow rectangular rods under the microscope and on heating turned brown at about 300°, but did not melt below 360°. (Found in air dried sample: C, 56·5; H, 3·4; and loss on drying *in vacuo* at 120°, 5·1; $C_{15}H_{10}O_7$, H_2O requires C, 56·2; H, 3·7; loss on drying 5·6%. Found in the dried sample C, 59·3; H, 3·2; $C_{15}H_{10}O_7$ requires C, 59·6 and H, 3·3%).

The colour reactions of nor-auranetin in alkaline buffer solutions were already described. In 5% sodium carbonate solution, the compound dissolved with a deep red colour which was stable for 12 hours. A small quantity of a blue precipitate separated in half an hour.

Nor-auranetin was acetylated by boiling with acetic anhydride and sodium acetate for 2 hours. The product crystallised from ethyl acetate-petroleum ether mixture as colourless needles melting at 220-21°. (Found: C, 58·3; H, 4·3; $C_{25}H_{20}O_{12}$ requires C, 58·6 and H, 3·9%.)

Fission of Auranetin

Auranetin (1 g.) was dissolved in absolute alcoholic potash (2 g. in 25 c.c.) and the solution refluxed for 6 hours on a water-bath. At the end of the period, the alcohol was removed under reduced pressure, water added and the alkaline solution acidified. The mixture was extracted with ether and the ether extract washed successively with 5% sodium bicarbonate and 5% sodium hydroxide. Each of the solutions was acidified, extracted with ether, the extract dried over anhydrous sodium sulphate and the solvent evaporated. From the bicarbonate solution was thus obtained anisic acid, its melting point being undepressed on admixture with an authentic specimen. The sodium hydroxide extract gave a pale yellow compound (ketone) which after recrystallisation from alcohol formed pale yellow rectangular prisms and melted at 116–17°. It gave a brown colour with alcoholic ferric chloride. (Found: OCH_3, 45·6; $C_{12}H_{16}O_6$, H_2O requires OCH_3, 45·2%.)

2-*Hydroxy*-3 : 4 : 5 : 4′-*tetramethoxy-chalkone*[5] (*II*)

2-Hydroxy-3 : 4 : 5-trimethoxy acetophenone[10] (I) (1 g.) and anisaldehyde (5 c.c.) were dissolved in alcohol (20 c.c.) and to the solution was added aqueous sodium hydroxide (10 g. in 10 c.c. of water) in small quantities while cooling in ice. The flask was then corked air-tight and left for 2 days with occasional shaking. The deep-red solution slowly solidified; water was then added and the solution extracted with ether to remove the unreacted aldehyde. It was acidified and again extracted with ether. The ether extract was washed with sodium bicarbonate solution to remove anisic acid, dried over anhydrous sodium sulphate and the solvent removed. A yellow oil was obtained which turned into a bright yellow crystalline solid on leaving in the refrigerator. It crystallised from alcohol as deep yellow rectangular plates, melting at 111–12°. (Bargellini and Oliverio give the melting point as 110°.)

3-*Hydroxy*-6 : 7 : 8 : 4 -*tetramethoxy flavone*[5] (III)

The above chalkone (1 g.) was dissolved in rectified spirit (25 c.c.) and aqueous sodium hydroxide (2N, 50 c.c.). To the red solution was added hydrogen peroxide (100 vols. 10 c.c.) in small quantities with cooling under the tap and vigorous shaking. A yellow solid separated during the preliminary stages which later went into the solution with a deep yellow colour. The excess of hydrogen peroxide was decomposed by heating on a water-bath and then the alcohol evaporated off. On cooling the remaining solution and acidifying it, the flavonol separated as a brown solid. Recrystallisation from rectified spirit yielded it as yellow rods which melted at 186-7°. Yield 0·4 g. (Bargellini and Oliverio record the m.p. as 187°.)

3:6:7:8:4'-*Pentamethoxy flavone*[5] (*IV*).

The 3-hydroxy compound (III) was methylated with dimethyl sulphate and freshly ignited potassium carbonate in dry acetone solution by refluxing on a water-bath for 10 hours. The acetone was distilled off, water added to the residue and the aqueous solution extracted with ether. On evaporating the ether solution a colourless solid remained which crystallised from alcohol as very pale yellow needles melting at 139–40°. Mixed melting point with the natural sample of auranetin was undepressed. (Bargellin and Oliverio[6] give the melting point of the pentamethoxy flavone as 141°.)

3:6:7:8:4'-*Pentahydroxy flavone.*[5]

The pentamethoxy flavone (0·5 g.) was dissolved in acetic anhydride (5 c.c.) and to the solution was added hydriodic acid (5 c.c. of 1·7 d.) with cooling. The mixture was gently boiled for half an hour, cooled and diluted with water saturated with sulphur dioxide. The precipitated deep yellow solid was filtered and thoroughly washed with aqueous sulphur dioxide. It was dried and recrystallised from acetic acid when it was obtained as bright yellow rectangular plates. The compound turned brown at about 300°, but did not melt below 360°. (Bargellini and Oliverio also recorded the same property).

It was identical with nor-auranetin in all its properties and colour reactions, including those given by alkaline buffer solutions. Its acetate crystallised from absolute alcohol as colourless needles melting at 220–21°. It did not depress the melting point of the acetate of nor-auranetin. (Bargellini and Oliverio give the melting point of the acetate as 216°.)

The above pentamethoxy flavone was subjected to alkaline hydrolysis as in the case of auranetin. The products were anisic acid and the 2-hydroxy-ω:3:4:5-tetramethoxy acetophenone (V) melting at 116–17°; the melting point was not depressed by admixture with the ketone obtained from auranetin. (Found: C, 52·4; H, 6·8; Loss on drying *in vacuo* at 100°, 6·9; $C_{12}H_{16}O_6$, H_2O requires C, 52·6; and H, 6·6; H_2O loss 6·6%.)

SUMMARY

Auranetin has been obtained pure. It is a colourless solid melting at 139–40° and is a pentamethoxy flavone. By alkali fission it yields anisic acid and a ketone containing four methoxyl groups. Direct comparison with compounds belonging to the types already known to occur in nature showed that it is quite novel and should belong to 6:7:8-methoxy type. This was confirmed by the preparation of 3:6:7:8-4'-pentamethoxy flavone and its derivatives and direct comparison. The ketone obtained

by the fission of the synthetic flavone is also identical with the one derived from auranetin. The contribution of citrus fruits to flavone chemistry and the biogenesis of the auranetin group are discussed.

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DIELECTRIC ANISOTROPY OF ROCKS

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(Communicatvd by Prof. S. Bhagavantam, F.A.SC.)

1. Introduction

Physical properties of rocks have assumed an importance in view of the recent developments in geophysical prospecting. Many of the properties have been widely studied, but generally without reference to the direction. Recently, Prasadarao[1] showed that there is anisotropy in the elastic behaviour of rocks. The ultrasonic velocity and the effective elastic constant have been found to be different in different directions. Koenigsberger[2] previously established experimentally that rock formations are in many cases not isotropic in their resistivity characteristics, and that differences as high as 20% may be observed in the values of some cleaved rocks in which determinations are made in directions parallel and perpendicular to the cleavage plane. Similar work on dielectric constants of rocks does not seem to have been reported. The author has accordingly undertaken a study of the same.

2. Experimental

The rock sections used in this investigation are the same as those employed by Prasadarao.[1] Jubbalpore marble (white), Hyderabad marble (grey), Rajaputana marble (pink), Bhima limestone, Kurnool limestone, Palnad limestone are the sedimentary types of rocks used. Keratophyre (Snowden, North Wales), norite (Kondapalle), chloritised dolerite (Hyderabad), leptynite (Kondavidu), eclogite (Scotland), Deccan trap (Rutlam), granite (Kondavidu), and pink coloured granite (Hyderabad) are the igneous types used. A full description of these rocks can be found in the communication referred to above.

Three mutually perpendicular sections are taken from each rock. One of them is parallel to the bedding plane or the cleavage plane. The other two are perpendicular to the above plane and also perpendicular to each other.

First of all the sections are dried at a temperature of 200° C. for four hours and the dielectric constants are then determined. Later, the sections are immersed in water for 15 minutes, taken out, and their surfaces wiped off.

They are left in a watch glass for over three days and the dielectric constants are again determined. When the sections are taken out, in the beginning they will have a larger moisture content but gradually they will lose some of the moisture and will finally retain a certain quantity, in equilibrium, depending upon the porosity of the section. So the dielectric constants of the rock sections are determined for this equilibrium moisture content. They may, to some extent, correspond to the dielectric constants of the rock *in situ* in different directions.

The method of determining the dielectric constants is the same as that developed and reported by the author[3] in an earlier communication. The determinations are made in the frequency range of 1 to 2 megacycles per second and at a temperature of 28° C.

3. RESULTS

The dielectric constants of the sections in the dry condition and with equilibrium moisture content are given in the Table. K_1 is the dielectric constant perpendicular to the plane of easy breakage. K_2, K_3 are constants in two mutually perpendicular directions and contained in the plane of easy breakage. D_1, D_2, D_3 are the densities of the corresponding sections.

Specimen	Condition	D_1	K_1	D_2	K_2	D_3	K_3
Jubbulpore marble (white) ..	dry	2·85	7·7	2·84	7·7	..	..
	moist		7·9		7·9		
Hyderabad marble (grey) ..	dry	2·67	6·2	2·72	8·3	2·73	8·3
	moist		6·8		9·4		9·0
Rajaputana marble (pink) ..	dry	2·71	8·5	2·70	8·7	..	..
	moist		8·7		8·8		
Bhima limestone ..	dry	2·70	8·8	2·72	8·5	2·72	8·4
	moist		10·4		12·2		12·4
Kurnool limestone ..	dry	2·70	8·4	2·66	8·5	2·68	8·6
	moist		10·2		12·5		12·2
Palnad limestone ..	dry	2·69	7·8	2·67	7·8	2·68	7·9
	moist		10·6		12·0		12·1
Keratophyre ..	dry	2·63	5·7	2·58	5·5	..	..
	moist		5·9		5·9		
Norite ..	dry	3·07	10·9	3·08	12·0	..	..
	moist		11·8		12·7		
Chloritised dolerite ..	dry	3·04	8·3	3·01	8·2	..	..
	moist		9·7		10·7		
Leptynite ..	dry	2·66	6·1	2·66	6·1	2·68	6·3
	moist		6·4		7·1		7·1
Deccan trap ..	dry	2·86	11·2	2·88	12·0	..	..
	moist		13·0		15·5		
Eclogite ..	dry	3·37	12·7	3·26	9·7	3·25	9·3
	moist		15·0		14·1		13·6
Kondavidu granite ..	dry	2·62	5·9	2·62	5·9	2·61	5·8
	moist		8·4		8·7		8·7
Hyderabad granite ..	dry	2·61	7·0	2·60	7·0	2·62	6·8
	moist		7·1		7·2		7·3

4. DISCUSSION OF RESULTS

In the dry condition, the dielectric constants of the different sections of a rock, except in a few cases, are nearly the same. Small differences of 0·1 or 0·2 may be due to slight inhomogeneities in the rock.

In the case of norite, eclogite, and Deccan trap the dielectric constants are high and the differences of K_1, K_2, K_3 of the same rock in the dry condition are conisderable. Norite and Deccan trap are known to contain iron ore as a constituent. Eclogite contains the mineral rutile which in the crystalline state has the high dielectric constants of 89 and 173 in the perpendicular and parallel directions. The densities of the sections giving higher values are larger. In the case of eclogite, where the differences in the dielectric constants are very high, the density differences are marked. The differences of K_1, K_2, K_3 in these cases may be due to the non-homogeneous distribution of the iron or rutile content.

When the rock sections hold some moisture, the dielectric constants increase in value. This increase depends upon the amount of water held, and consequently the porosity. With the Jubbalpore and Rajaputana marbles the increases in the values are very small, indicating that the moisture those marbles can hold in equilibrium is small. The increase in the case of Hyderabad marble is more.

In the case of limestones, the values with the equilibrium moisture content are up to 50% more than the dry values. In the case of all limestones used, the values K_2, K_3 (moist) are nearly the same, whereas K_1 (moist) is different. So the increase in the dielectric constant with moisture perpendicular to the bedding plane is smaller than that parallel to the plane. This result is in consonance with Koenisberger's observation that the conductivity of the rock perpendicular to the bedding or cleavage plane is in some cases less than that parallel to the plane. Prasadarao found that the effective elastic constant perpendicular to the bedding plane is more than that parallel to the plane. So in the direction in which the elastic constant is less, the change of dielectric constant with moisture, and the conductivity are more.

In the case of the igneous rocks also the increase in the dielectric constant with moisture perpendicular to the cleavage plane is less than that parallel to the plane. The direction of the larger change in the dielectric constant with moisture happens to be the direction of the smaller elastic constant.

Prasadarao found that of all rocks, eclogite behaved elastically isotropic within 1%. But it happens to be the one which shows the maximum variation in K_1, K_2, K_3 in the dry condition. That is likely to be due to the inhomogeneous distribution of rutile. The changes in the values of K_1, K_2, K_3 with moisture are nearly the same.

5. SUMMARY

The dielectric constants of six sedimentary rocks and eight igneous rocks are determined. A directional study is made by cutting three mutually perpendicular sections, one of them being parallel to the plane of easy breakage. In the dry condition, the dielectric constants in different directions are found to be nearly the same for most cases. In the case of a few like eclogite, norite and deccan trap which have iron ores or rutile as constituents, there are differences in the values in different directions in the dry condition.

When the sections contain an equilibrium moisture content the values are found to be markedly different in different directions. The increase in the dielectric constant with moisture is found to be less perpendicular to the bedding or cleavage plane than that parallel to the plane.

The author wishes to express his grateful thanks to Prof. S. Bhagavantam for his keen interest in the above investigation. His thanks are due to Mr. G. H. S. V. Prasadarao for lending the cut sections of the rocks.

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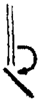
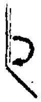
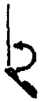
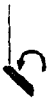
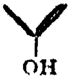
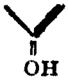
P. 379 in Structural Formula XIX, *read*  *for* 

P. 379 in Structural Formula XX, *read*  *for* 

P. 381 in Structural Formula of pedicinin *read*  *for* 

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NUCLEAR OXIDATION IN THE FLAVONES AND RELATED COMPOUNDS

Part XIV. Constitution of Quercetagitrin

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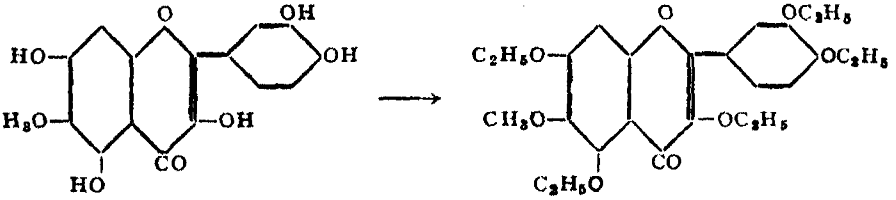
Received July 1, 1948

Two important species of the Marigold, *Tagetes erecta*[1] and *Tagetes patula*[2] have been examined in the past with regard to their flower pigments. The difference in species is clearly indicated in the nature of the colouring matter present. The first contains mainly the monoglucoside, quercetagitrin along with some quantity of its aglucone, quercetagetin. On the other hand the flowers of *Tagetes patula* yield only patuletin which is a mono-methyl ether of quercetagetin. Thus the close botanical relationship between the two species and at the same time their species difference is paralleled on the chemical side. The pigments of both flowers are based on quercetagetin, one containing the monoglucoside and the other the monomethyl ether.

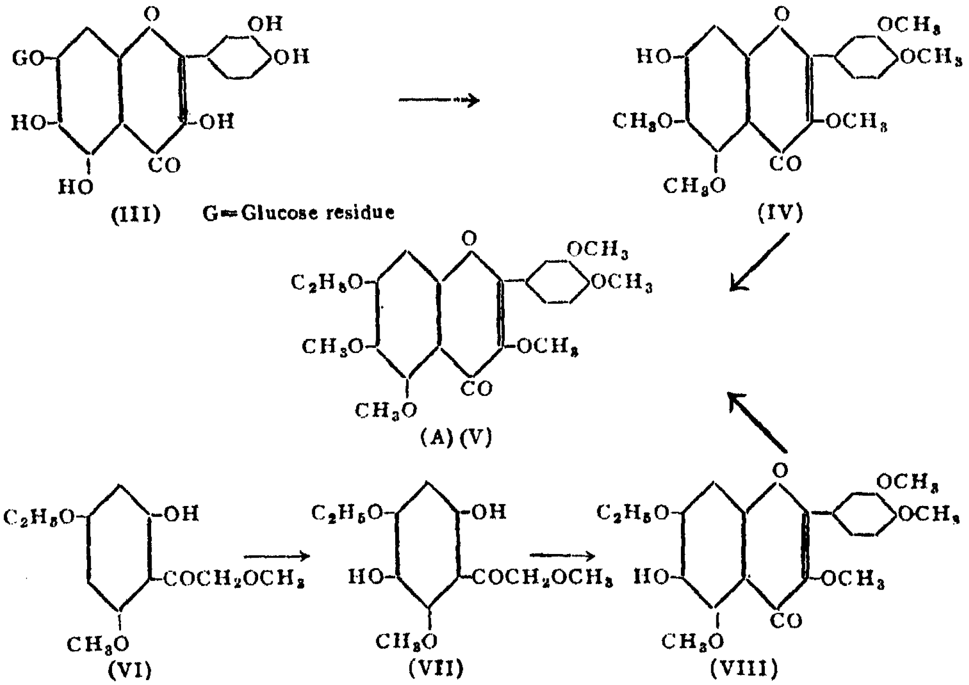
The constitution of patuletin was first surmised[3] as the 6-methyl-ether (I) from its properties and reactions and it was later confirmed[4] definitely by the unequivocal synthesis of its penta-ethyl ether (II).



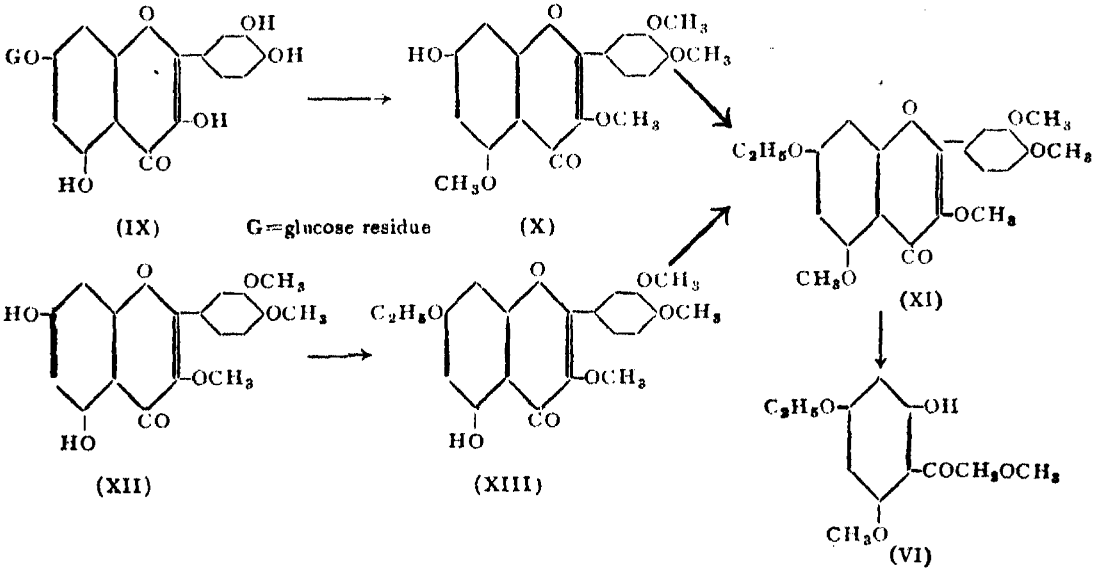
(I) (II)

With regard to quercetagitrin, its constitution as the 7-monoglucoside was originally arrived at only by the elimination of other possibilties.[1] After the complete methylation of the glucoside through the acetate and subsequent hydrolysis, a pentamethyl quercetagetin was obtained which gave, on decomposition with alkali, veratric acid thus eliminating the possibility of existence of the free hydroxyl group in the side phenyl nucleus. Comparison with the already known 5-hydroxy compound showed that it was different and eliminated this position also from consideration. The lack of prominent ferric chloride colour showed that there was no free hydroxyl even in the 3-position. Out of the two still left, the position 7 (formula IV) was considered to have the free hydroxyl group because the allyl ether of the compound underwent Claisen migration smoothly. This would not have been possible if the 6-position was concerned. But no confirmation by synthesis was provided for the constitution of this pentamethyl quercetagetin and eventually for the glucoside, quercetagitrin. This has now been supplied by experiments described in this paper.

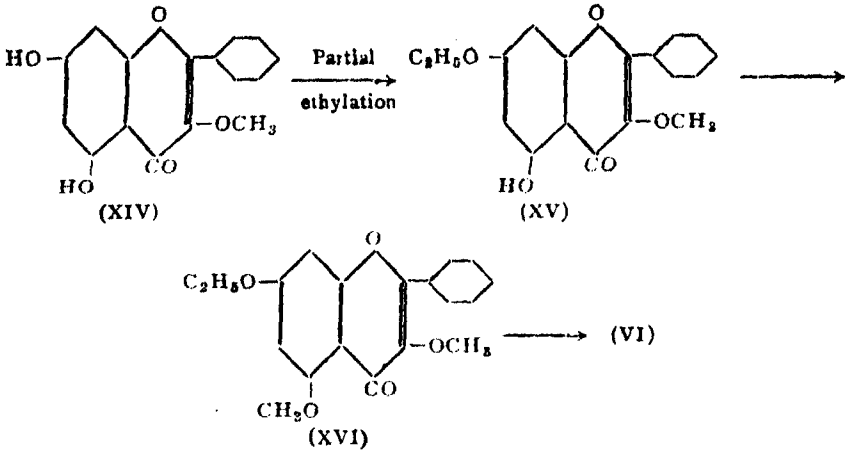
Quercetagitrin has now been more conveniently methylated using excess of dimethyl sulphate and potassium carbonate in acetone medium. The pentamethyl quercetagetin obtained by the hydrolysis of the methylated glucoside has been further ethylated and this mixed ether (A) has been shown to be identical with a synthetic sample of 7-ethoxy-3 : 5 : 6 : 3′ : 4′-pentamethoxy flavone (V). The starting point for this synthesis is 2-hydroxy-4-ethoxy-ω : 6-dimethoxy acetophenone (VI) and the stages are given by the following formulæ. Thus it is confirmed that the pentamethyl quercetagetin has formula (IV) and quercetagitrin formula (III).



The above mentioned starting material (VI) has been most conveniently obtained from quercimeritrin, the well-known monoglucoside of quercetin. Its constitution as a 7-glucoside (IX) was originally advanced by Attree and Perkin[5] (see also Rao and Seshadri[6]) by a process of elimination. They showed that the derived tetramethyl quercetin did not have the free hydroxyl group in the side phenyl nucleus by a study of its decomposition products and that it was not in the 3 or the 5-position by comparison with the required synthetic compounds. No confirmation of the constitution (X) by synthesis has been made so far. This has now been done by the ethylation of the tetramethyl quercetin and by the synthesis of the resulting mixed ether (XI) by a straightforward method. 3 : 3′ : 4′-*O*-trimethyl quercetin (XII)[7] which is readily obtained by the Allan-Robinson condensation of ω-methoxy-phloracetophenone with the anhydride and sodium salt of veratric acid, is partially ethylated using just one mol. of ethyl iodide and the product (XIII) is a monoethyl ether whose reactions indicate that the resistant 5-hydroxyl group is still free. Final methylation with excess of dimethyl sulphate yields the required mixed ether of quercetin (XI). The various stages are indicated by the following formulæ:



Fission using alcoholic alkali of the above mixed ether (XI) obtained either from quercimeritrin or by the synthetic method yielded besides veratric acid the required 2-hydroxy-4-ethoxy-ω : 6-dimethoxy acetophenone (VI) and this was employed as the starting material for the synthesis of the above mentioned pentamethyl-monoethyl quercetagetin. As a purely synthetic method of obtaining this ketone, the synthesis of *O*-7-ethyl-3 : 5-dimethyl galangin (XVI) and its fission with alcoholic alkali has also been carried out. This is far more convenient than preparing the quercetin derivative synthetically.



The above experiments emphasise the relationship between quercimeritrin and quercetagitrin, both being 7-glucosides. Further from the results it will be clear that the species difference between *T. erecta* and *T. patula* is not only exhibited in the way a hydroxyl group is protected but this is also exhibited in the particular position involved, 7- in the glucoside and 6- in the methyl ether. This choice of the position for the glucoside formation and methylation in the case of 5:6:7-hydroxy-flavones and flavonols is rather interesting. As somewhat parallel cases may be mentioned the derivatives of scutellarein and baicalein. In their partial methyl ethers the 6-position is used in preference to 7. For example, the 6-methyl ether of baicalein (oroxylin-A) is found in *Oroxylum indicum* and the 6:4′-dimethyl ether of scutellarein occurs in *Linaria vulgaris*. Regarding the glucuronides, baicalin and scutellarin Armstrong and Armstrong in their well-known monograph on glycosides[8] state that the glucuronic acid is in both cases thought to be attached in position 6. No evidence is however mentioned in support of this opinion. On the other hand the experiments of Shibata and Hattori[9] would show that the constitution of baicalin should be as the 7-glucuronide of baicalin.

EXPERIMENTAL

Quercetin-tetramethyl-ether (X) *from Quercimeritrin.*

Quercimeritrin required for this work was obtained from the flower petals of the Cambodia cotton plant (*Gossypium hirsutum*).[10] It (1·0 g.) was suspended in dry acetone (150 c.c.) and anhydrous potassium carbonate (5 g.) and dimethyl sulphate (3 c.c.) were added and the mixture was heated under reflux for a period of 30 hours. The potassium salts were filtered and washed with warm acetone. From the filtrate the solvent was distilled off and water added to the residue. The methyl ether separated as a semi-solid mass; it gave no colour with alcoholic ferric chloride. It was directly boiled with 7% aqueous sulphuric acid for two hours. It first went into solution and a colourless solid soon separated out. The product was filtered and washed with water. On crystallisation from alcohol the tetramethyl ether was obtained as narrow rectangular plates, melting at 284–85°; Attree and Perkin[6] and Rao and Seshadri[6] recorded the same melting point. It dissolved in aqueous sodium hydroxide to give an yellow colour but did not give any colour with alcoholic ferric chloride. Yield, 0·4 g. (Found: C, 63·7; H, 5·4; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%.) Its acetate melted at 174–75°.

Monoethyl-tetramethyl-quercetin (XI)

The above tetramethyl quercetin (0·2 g.) was dissolved in dry acetone (50 c.c.), freshly ignited potassium carbonate (5 g.) and ethyl iodide (0·5 c.c.) added and the mixture refluxed for 15 hours. The potassium salts were filtered and washed with warm acetone. On removing the solvent from the filtrate and adding water, the ethyl ether separated as a colourless solid. It crystallised from ethyl acetate as broad rhombohedral plates and prisms melting at 159–60°. It was insoluble in aqueous sodium hydroxide and did not give any colour with alcoholic ferric chloride. The mixed melting point with a synthetic sample of 7-ethoxy-3: 5: 3′: 4′-tetramethoxy-flavone was undepressed. (Found: C, 65·6; H, 5·8; $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%).

7-Ethoxy-5-hydroxy-3: 3′: 4′-trimethoxy-flavone (XIII)

5: 7-Dihydroxy-3: 3′: 4′-trimethoxy-flavone[7] (0·5 g.) in dry acetone (50 c.c.) was treated with anhydrous potassium carbonate (5·0 g.) and ethyl-iodide (1·1 mol.; 0·3 c.c.) and refluxed for 8 hours. After filtration, the solution was concentrated whereby the crude partially ethylated compound was obtained as a pale yellow solid. It crystallised from absolute alcohol as narrow rectangular plates (pale yellow) melting at 134–35°. It gave a reddish-brown colour with alcoholic ferric chloride, was sparingly soluble in aqueous sodium hydroxide and dissolved in concentrated sulphuric acid to give a bright yellow solution. Yield, 0·4 g. (Found: C, 64·7; H, 5·0; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%).

7-Ethoxy-3: 5: 3′: 4′-tetramethoxy-flavone (XI)

The above 5-hydroxy compound (0·2 g.) was further methylated in dry acetone (50 c.c.) solution using anhydrous potassium carbonate (5 g.) and freshly distilled dimethyl sulphate (0·5 c.c.) and heating under reflux for

20 hours. The product was readily obtained as a colourless solid. It crystallised from ethyl acetate as broad rectangular plates melting at 158–60°. Yield, 0·2 g. (Found: C, 65·1; H, 5·3; $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%). It was identical with the monoethyl-tetramethyl quercetin obtained from quercimeritrin.

Pentamethyl quercetagetin from quercetagitrin (IV)

The glucoside required for this purpose was isolated from the flowers of *Tagetes erecta* using a modification of the method adopted by Rao and Seshadri.[1] The alcoholic extract of the petals was concentrated removing as much alcohol as possible. The residue was treated with excess of water, heated and resinous matter filtered off. The clear solution was concentrated to a small bulk and repeatedly extracted with ether in order to remove quercetagetin. When the aqueous solution was allowed to stand saturated with ether, the glucoside separated in the course of a few weeks. It was filtered and washed with ether and recrystallised from pyridine.

It (0·5 g.) was methylated as in the case of quercimeritrin using dry acetone (100 c.c.), anhydrous potassium carbonate (7 g.) and freshly distilled dimethyl sulphate (3 c.c.) and refluxing the mixture for 30 hours. When the filtrate was concentrated to remove the solvent and water added no solid separated. Hence the solution was rendered 7% acid by the addition of the requisite amount of sulphuric acid and gently boiled for 2 hours, when the aglucone separated out slowly. It was filtered and washed with water. On crystallisation from alcohol the monohydroxy compound was obtained as colourless long plates and needles, melting at 234–35° (Rao and Seshadri[1]). Yield, 0·2 g.

Monoethyl-pentamethyl-quercetagetin (A)

The above pentamethyl ether (0·15 g.) was ethylated using dry acetone (50 c.c.), anhydrous potassium carbonate (3 g.) and ethyl iodide (0·3 c.c.) and refluxing the mixture for 20 hours. The potassium salts were filtered off and washed with warm acetone. When the filtrate was concentrated to remove the solvent and water added, a brown sticky solid separated out. It was left in the ice-chest overnight when the product came out as an amorphous powder. Crystallisation from aqueous alcohol yielded colourless plates melting at 127–28°. The melting point was not depressed by admixture with a synthetic sample of 7-ethoxy-pentamethoxy flavone (V). Yield, 0·15g. It was insoluble in aqueous sodium hydroxide and did not give any colour with alcoholic ferric chloride. (Found: C, 63·2; H, 5·6; $C_{22}H_{24}O_8$ requires C, 63·5; H, 5·8%).

2-*Hydroxy*-4-*ethoxy*-ω: 6-*dimethoxy-acetophenone* (*VI*)

7-Ethoxy-3 : 5 : 3′ : 4′-tetramethoxy-flavone obtained from quercimeritrin or synthetically (1·0 g.) was treated with absolute alcoholic potash (40 c.c., 8%) and the solution refluxed for 6 hours. As much of the alcohol as possible was removed under reduced pressure and the remaining solution diluted with water. It was then rendered acidic with dilute sulphuric acid and ether extracted. The ether extract was shaken with aqueous sodium bicarbonate in order to remove veratric acid and then evaporated when the ketone separated as a colourless solid. Crystallisation from alcohol yielded it as thin rectangular plates and needles melting at 105–6°. It gave a reddish brown colour with alcoholic ferric chloride and dissolved in aqueous sodium hydroxide to give an yellow solution. Yield 0·5 g. (Found: C, 60·0; H, 6·5; $C_{12}H_{16}O_5$ requires C, 60·0; H, 6·7%.)

2 : 5-*Dihydroxy*-4-*ethoxy*-ω : 6-*dimethoxy-acetophenone* (*VII*)

To a stirred solution of the above ketone (1·0 g.) in aqueous sodium hydroxide (1·0 g. in 15 c.c.) was added dropwise a solution of potassium persulphate (1·2 g. in 30 c.c. of water) in the course of two hours, the temperature being kept at 15–20°. After 24 hours the brown aqueous solution was neutralised with dilute hydrochloric acid to congo red and ether extracted to remove the unreacted ketone. To the aqueous solution was then added concentrated hydrochloric acid (20 c.c.) and sodium sulphite (2 g.) and the mixture heated in a boiling water-bath for half an hour. It was then cooled and extracted with ether. On distilling off the ether a viscous liquid was obtained which did not solidify even after leaving in the refrigerator for a number of days. Hence it was employed directly for the subsequent condensation. Yield, 0·25 g.

It gave a greenish brown colour with alcoholic ferric chloride and an yellow solution with aqueous sodium hydroxide.

7-*Ethoxy*-3 : 5 : 6 : 3′ : 4′-*pentamethoxy flavone* (*V*)

An intimate mixture of the ketone (VII) (1·0 g.), veratric anhydride (6·0 g.) and sodium veratrate (2·5 g.) was heated under reduced pressure at 170–80° for 4 hours. The dark brown product was dissolved in hot alcohol (25 c.c.) and refluxed with an aqueous solution of potassium hydroxide (3 g. in 3 c.c. of water) for 30 minutes. The solvent was removed under reduced pressure and the residue dissolved in water. After saturation with carbon dioxide the solution was extracted with ether. On evaporating the ether solution the flavone was obtained as a viscous oil. It gave an olive green colour with ferric chloride indicating partial demethylation in the

5-position and an alcoholic solution of the substance gave a deep red colour with magnesium and hydrochloric acid. It was directly employed for the subsequent methylation by dissolving in dry acetone (30 c.c.) and boiling with anhydrous potassium carbonate (6 g.) and dimethyl sulphate (2·5 c.c.) for 20 hours. After filtration, the filtrate was concentrated and treated with water. The semi-solid mass thus obtained was taken up in ether and the ether solution evaporated. The residue was crystallised from benzene-petroleum ether when the 7-ethoxy-pentamethoxy flavone was obtained as rectangular plates melting at 127–28°. Yield, 0·5 g. It was insoluble in aqueous sodium hydroxide and did not give any colour with alcoholic ferric chloride. (Found: C, 63·6; H, 5·8; $C_{22}H_{24}O_8$ requires C, 63·5; H, 5·8%.)

7-Ethoxy-5-hydroxy-3-methoxy-flavone (XV)

Galangin-3-methyl ether[11] (2·0 g.) in dry acetone (100 c.c.) was treated with anhydrous potassium carbonate (2 g.) and ethyl iodide (1 mol., 1 c.c.) and the contents were refluxed for 6 hours. The potassium salts were filtered and washed with warm acetone. On concentrating the filtrate a semi-solid mass was obtained which when treated with a little alcohol yielded a yellow solid. It crystallised from alcohol as narrow rectangular plates (yellow) melting at 125–6°. It gave a reddish-brown colour with alcoholic ferric chloride. Yield, 1·5 g. (Found: C, 69·3; H, 5·1; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%.)

7-Ethoxy-3: 5-dimethoxy flavone (XVI)

The above 5-hydroxy compound (0·5 g.) was methylated in dry acetone (50 c.c.) with excess of dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (5 g.) by boiling the mixture for 10 hours. The methyl ether crystallised from alcohol as fine needles melting at 128–29°. It did not give any colour with alcoholic ferric chloride and was insoluble in aqueous sodium hydroxide. Yield, 0·4 g. (Found: C, 69·5; H, 5·2; $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%).

This flavone (1·0 g.) was subjected to fission using absolute alcoholic potash (40 c.c., 8%) and the product worked up just as in the case of the quercetin derivative. 2-Hydroxy-4-ethoxy-ω: 6-dimethoxy acetophenone was obtained in an yield of 0·6 g.

SUMMARY

Synthetic confirmation for the constitution of quercetagitrin is provided. The pentamethyl-quercetagetin obtained by the complete methylation and hydrolysis of the glucoside is finally ethylated and the product shown to be identical with a synthetic sample of 7-ethoxy-3: 5: 6: 3′: 4′-pentamethoxy

flavone (V) made from 2-hydroxy-4-ethoxy-ω:6-dimethoxy-acetophenone (VI) using oxidation with persulphate, Allan-Robinson condensation and final methylation as stages. The ketone (VI) is conveniently made by the alkali fission of *O*-7-ethyl-3:5:3′:4′-tetramethyl-quercetin obtained from quercimeritrin. This mixed ether of quercetin is also made independently by synthesis and this constitutes a synthetic confirmation of the constitution of quercimeritrin. Further, the transformations show the relationship between quercimeritrin and quercetagitrin as 7-glucosides. The most convenient synthetic route for the ketone (VI) is through the galangin derivative (XVI).

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INFLUENCE OF TEMPERATURE ON THE RAMAN SPECTRA OF CRYSTALS

Part III. Barytes

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1. Introduction

Although the Raman spectrum of barytes has been studied by a number of authors (Rasetti, 1932; Balakrishnan, 1941; Roopkishore, 1942; Krishnan, 1946 and others), its variation with temperature has not been investigated so far. In continuation of the work on calcite and quartz reported earlier in the *Proceedings* (Narayanaswamy, 1947 *a*, *b*) the author has now studied the influence of temperature on the Raman spectrum of barytes and the results are reported in this paper.

2. Experimental

A transparent piece of barytes (1″ × 1″ × ½″) was used for these investigations. The experimental arrangements for obtaining the Raman spectra at different temperatures were the same as described in Part I of this series (Narayanaswamy, 1947 *a*). The spectra were excited by the λ 2536 resonance radiation of a quartz mercury arc and were photographed with a Hilger E3 medium quartz spectrograph. The variations in the position and width of the principal Raman lines were studied with the crystal held at 85, 300, 408, 513, 588, 698, 818 and 923° K. respectively. A fine slit 0·025 mm. wide was employed in order to obtain good resolution and exposures of the order of 3 hours were required to get reasonably intense spectrograms. With the large E1 spectrograph, two photographs, one with the crystal at room temperature and the other with the crystal held at 770° K. were taken in juxtaposition with the help of a Hartmann diaphragm to demonstrate clearly the effect of temperature on the various Raman lines.

3. Results

Typical spectrograms of the Raman spectrum of barytes with the crystal held at different temperatures are reproduced in Fig. 1 (Plate I). The E1 photograph is reproduced in Fig. 2 (Plate I). In Table I, the measured frequency shifts of the principal Raman lines at various temperatures from that of liquid air to 923° K. are given. The total variation in their positions from room temperature to the highest attained, and the proportional change $\chi = 1/\nu . d\nu/dT$ for each of the important Raman lines are put down in Table II along with their measured widths at room temperature and at 923° K.

TABLE I

Variations in frequency shift of the principal Raman lines in barytes with temperature

$\nu_{85^\circ K}$ in cm^{-1} liq. air temp.	ν_{300° in cm^{-1} room temp.	ν_{408° in cm^{-1}	ν_{513° in cm^{-1}	ν_{598° in cm^{-1}	ν_{698° in cm^{-1}	ν_{818° in cm^{-1}	ν_{923° in cm^{-1}
75	**74·5**	74·2	73·1	71·7	71·5	71·0	69·5
90·2	**89·0**	88·6	88·4	88·0	88·0	87·5	87·0
128·5	**127·0**	126·8	126·0	124·5	123·1	121·2	119·5
151·9	**150**	148·7	146·7	144·6	143·2	142·0	139·1
193	**190**	187·1	184	181·4	178·5	174·2	169·0
453	**452·0**	456	456	455·8	454	452·4	451
463·8	**462**						
648	**647**	644·1	643·2	642·6	641·5	642·5	641·2
991	**989**	986·3	983·0	981·4	979·1	976	972·0
1088	**1084**	1082	1079·5	1077·6	1074·3	1072	1067·0
1105	**1104**	1101·5	1098·5	1096·7	1094·0	1091	1087
1144·6	**1142**	1138·9	1136·4	1134·1	1130·6	1126·3	1121
1168·5	**1167**	1165·5	1162	1159	1156·7	1152·4	1147·5

TABLE II

Total variations in frequency shift and width of the principal Raman lines and their proportional change χ

Centre of Raman line at 300°K. ν_{300° in cm^{-1}	Centre of Raman line at 923°K. ν_{923° in cm^{-1}	Shift $d\nu$ in cm^{-1}	Proportional change $\chi = 1/\nu \cdot \frac{d\nu}{dT}$	Breadth of line at 300°K. in cm^{-1}	Breadth of line at 923°K. in cm^{-1}
74·5	69·5	4·8	$105·5 \times 10^{-6}$	4·2	8·0
89	87·0	2·0	36·1 ,,	5·2	8·5
127	119·5	7·5	95 ,,	4·1	12·0
150	139·1	10·9	116·7 ,,	5·0	12·5
190	169·0	21·0	177·4 ,,	5·9	20
452	451			5·2	36·1
462				8·2	
647	641·2	5·8	14·3 ,,	5·0	7·0
989	972·0	17·0	27·6 ,,	11·5	31·0
1084	1067	17·0	25·3 ,,	4·9	16·5
1104	1087	17·0	24·7 ,,	4·4	17·0
1142	1121	21·0	29·4 ,,	13·0	25·0
1167	1147·5	19·5	26·8 ,,	7·4	19·0

From Table I, it may be noticed that on cooling the crystal to liquid-air temperature, the Raman lines show an appreciable increase in frequency shift. The increase is found to be greatest in the 190 cm.$^{-1}$ and the 1084 cm.$^{-1}$ Raman lines. That all the lines appear sharper at liquid air temperature will be evident from Fig. 1 (Plate I). With rising temperature, all the Raman lines shift more and more towards the exciting line. The extent of this diminution in frequency shift is, however, not the same for all the lines. For instance, when the temperature of the crystal is increased from

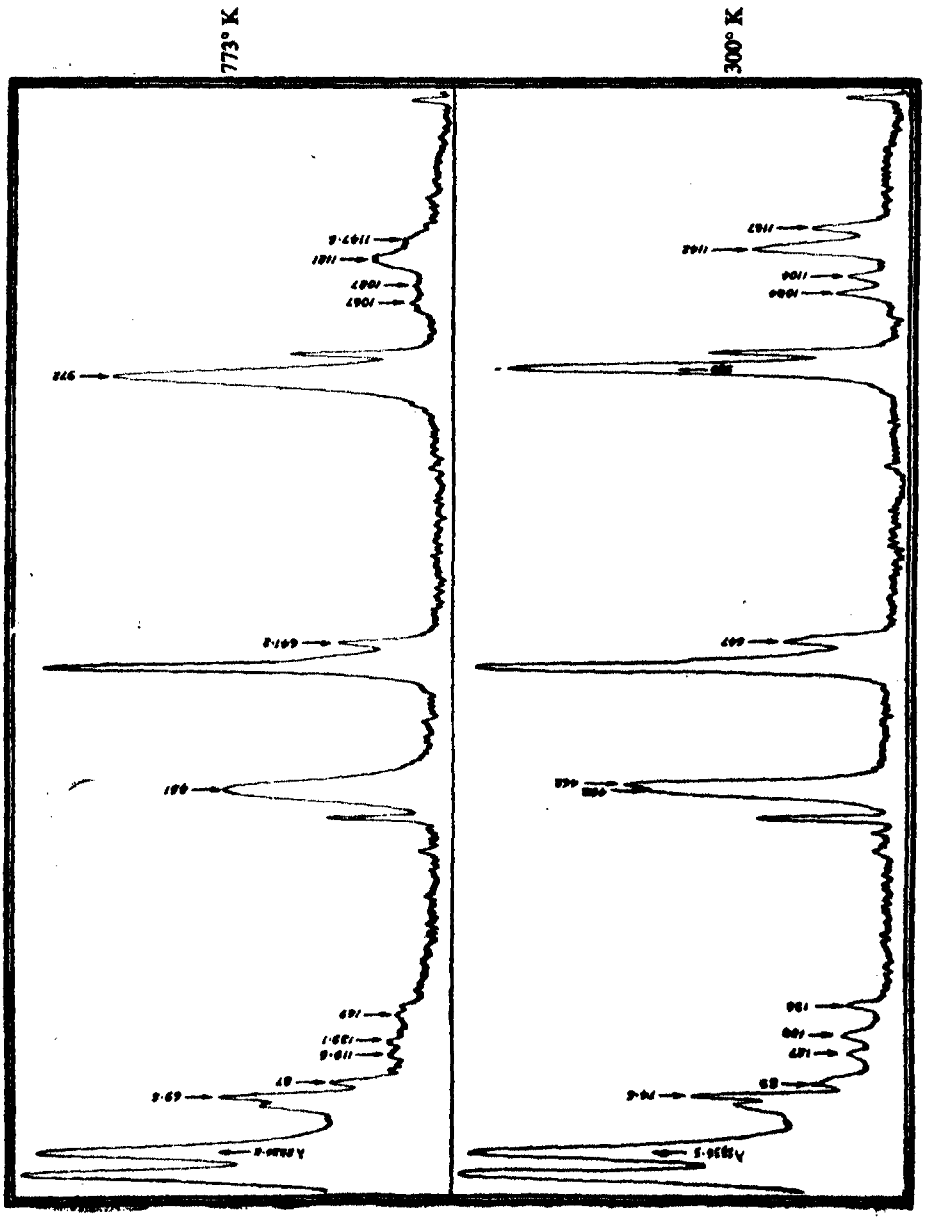

Fig. 3. Microphotometer curve of E1 spectrogram taken with Hartmann diaphragm, showing the variations in position and width of the principal Raman lines in barytes.

300° to 923° K., the 89 cm.$^{-1}$ Raman line shifts towards the exciting line by 2 cm.$^{-1}$ only, whereas for the same increase in temperature, the 190 cm.$^{-1}$ line shifts by about 20 cm.$^{-1}$ The internal frequencies also shift appreciably, the only exception being the 647 line which undergoes only a small shift. The total variations in the position and width of the different Raman lines can be seen vividly in the microphotometer curve of the E1 spectrogram reproduced in Fig. 3. The changes are also represented graphically for some of the important Raman lines in Fig. 4.

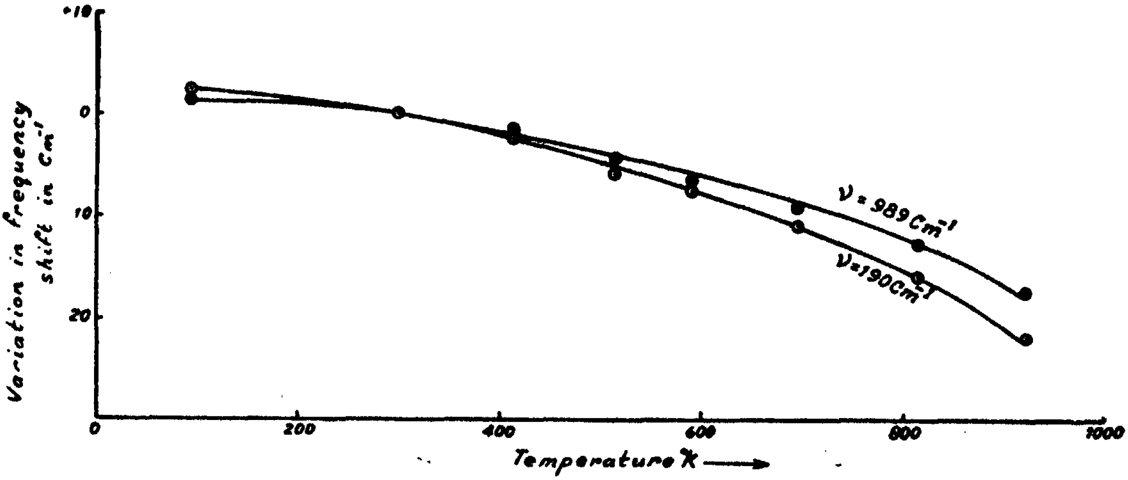

FIG. 4. Temperature dependence of the position of 190 cm.$^{-1}$ and 989 cm.$^{-1}$ Raman lines

It will be seen from Fig. 1 (Plate I) that as the temperature of the crystal is increased, the Raman lines broaden out considerably. This increase in the width of the lines is different for the various Raman lines. The lattice lines at 74·5 and 89 cm.$^{-1}$ for instance, remain appreciably sharp even at very high temperatures, while the other lattice lines broaden out greatly. The maximum increase in width is shown by the lattice line at 190 cm.$^{-1}$ and the internal frequencies at 989 and 1142 cm.$^{-1}$ The 647 cm.$^{-1}$ line exhibits the least amount of broadening. The 452–462 cm.$^{-1}$ doublet becomes a broad band as soon as the crystal attains temperatures higher than the room temperature. At very high temperatures, the lattice lines at 127 and 150 cm.$^{-1}$ as also the 1084 and 1104 cm.$^{-1}$ lines merge into one another. The 1167 cm.$^{-1}$ Raman line becomes very diffuse at high temperatures.

4. DISCUSSION

Spectrum of the SO_4 ion.—In the free state, the SO_4 ion has only 4 distinct modes of vibration whose frequency shifts are 454 (2), 622 (3), 983 (1) and 1106 (3) cm.$^{-1}$, the figures in brackets being their respective degeneracies. At room temperature, with the disappearance of degeneracy, the spectrum of barytes crystal shows actually 11 frequency shifts attributable to the SO_4 group, 9 of which are due to the splitting up of the 4 distinct modes of oscillation characteristic of the SO_4 ion into components in the crystal and the remaining two arise from the Fermi splitting of two of the fundamental frequencies (Krishnan, *loc. cit.*). With rising temperature of the crystal, however, it is observed that the 452 and 462 cm.$^{-1}$ lines which are the two components into which the 454 (2) fundamental mode of oscillation of the SO_4 group splits, merge into one another and become indistinguishable as separate entities. Similar tendencies are also observed in the case of the 1094, 1142 and 1167 cm.$^{-1}$ Raman lines which are the components of the 1106 (3) fundamental mode, at higher temperatures. These observations tempt us to remark that with increasing temperature, the degeneracies of the modes of oscillation of the SO_4 group are gradually restored and the vibrating ion as a whole tends to attain greater symmetry.

The diminution in frequency shift of the Raman line with increasing temperature of the crystal is not uniform for equal changes in temperature. This will be clear if we consider the proportional change, χ *i.e.*, $1/\nu \cdot d\nu/dT$ for the different ranges of temperature for each of the Raman lines. For the 150 cm.$^{-1}$ lattice line for example, χ for the temperature range 85° to 300° K. is 58×10^{-6} whereas for the range 698° to 923° K. it is 127×10^{-6}. For the 1067 cm.$^{-1}$ line, the values are 6×10^{-6} and 35×10^{-6} for the same ranges of temperature. It will be seen that the proportional change is greater at high temperatures than at low temperatures, the value of χ increasing with rising temperature. This is clearly shown in Fig. 4 where the temperature frequency shift curve exhibits a greater slope at higher temperatures, and tends to flatten at low temperatures although it does not actually become so.

The mean χ values for the various Raman lines for the temperature range 300–923° K. are given in Table II. The value of χ ranges from $14 \cdot 3 \times 10^{-6}$ to $177 \cdot 4 \times 10^{-6}$. It will be easily seen that χ for the different lattice lines is of the same order of magnitude indicating that the lattice forces are temperature sensitive to more or less the same extent. The only exception is the 89 cm.$^{-1}$ line which shows a very low temperature sensitivity. The different internal frequencies also have χ values which are of the same order of magnitude, *i.e.*, about 25×10^{-6} which shows that the internal oscillations of the SO_4 ion are affected to nearly the same extent by temperature variations. Here again, the 647 cm.$^{-1}$ line shows a very low temperature sensitivity. As was observed in the case of calcite by the author (*loc. cit.*), the lattice frequencies exhibit greater χ values than the internal frequencies, showing that the former are much more temperature sensitive than the latter.

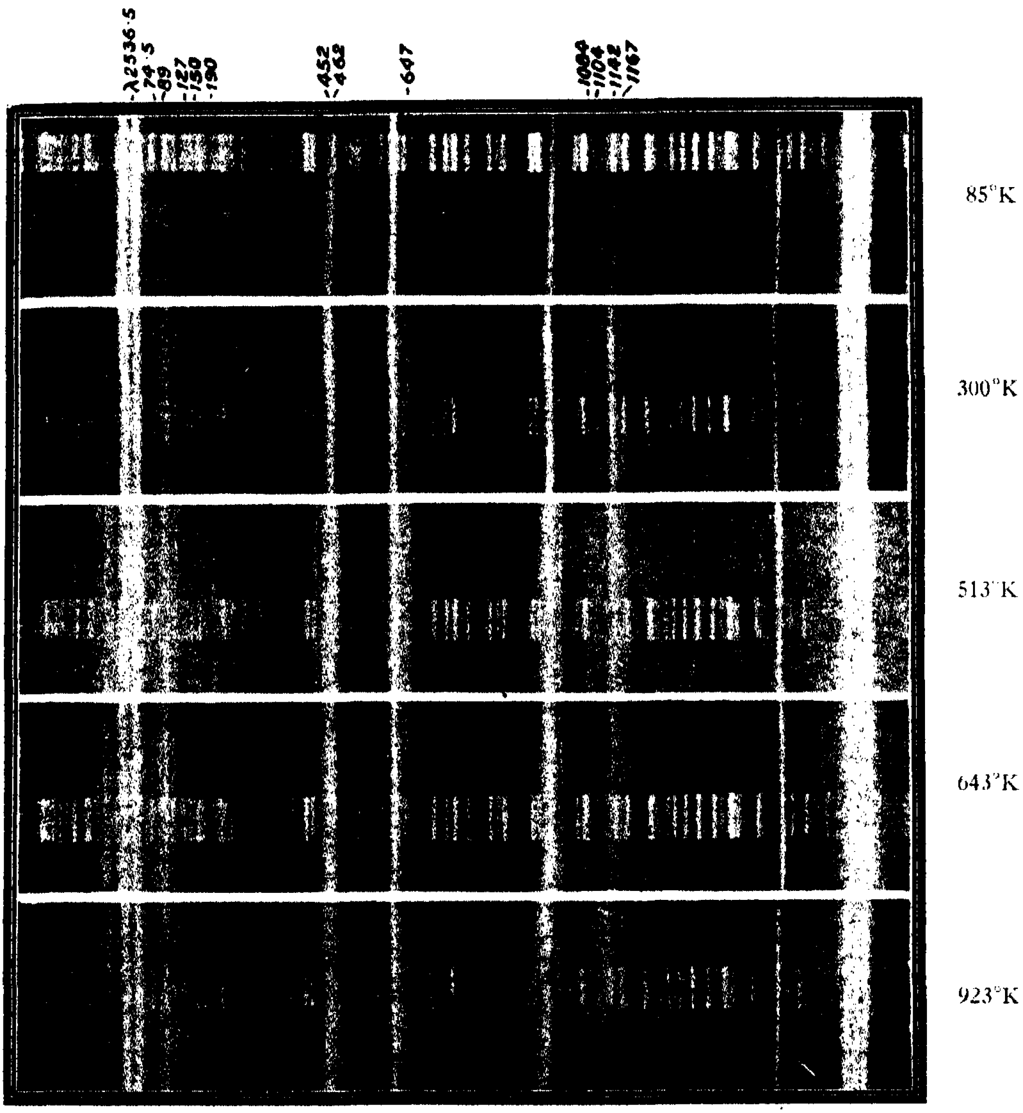

FIG. 1. Raman spectrum of barytes at various temperatures taken with E 3 spectrograph

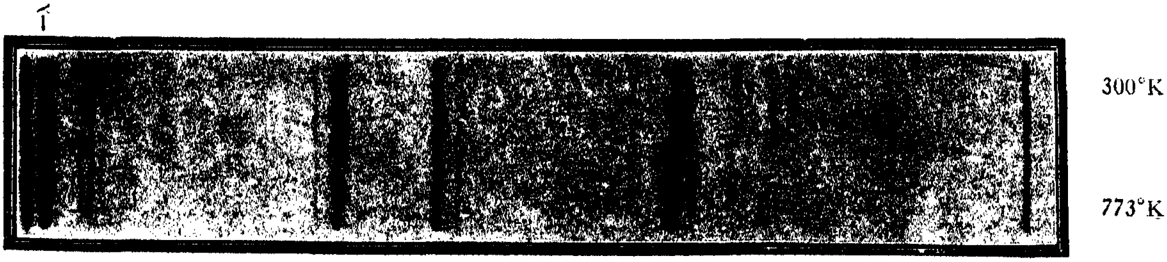

FIG. 2. Raman spectrum of barytes taken with E 1 spectrograph using Hartmann diaphragm

Regarding the width of the Raman lines, it is interesting to observe that those lines which do not show appreciable temperature variations in frequency shift like the 89 and 647 cm.$^{-1}$ Raman lines, do not also broaden out perceptibly. These lines remain sharp even at very high temperatures, whereas the lines which broaden out enormously, *e.g.*, 190 and 989 cm.$^{-1}$ Raman lines, also show considerable diminution in frequency shift, the variations in position and width being of comparable order of magnitude. The increase in width is, however, greater in all cases than the decrease in frequency shift. These observations tend to support the idea that the diminution in frequency shift and the increase in width of the Raman lines observed in crystals with rising temperature are closely connected and interrelated, as indicated by Sir C. V. Raman (1947). It may be also remarked that the peak intensity of the different Raman lines undergoes a notable diminution with increasing temperature (see Fig. 3).

In conclusion, the author wishes to express his heartfelt thanks to Prof. Sir C. V. Raman, KT., F.R.S., N.L., for his keen interest and inspiring guidance in the course of this investigation.

SUMMARY

The Raman spectrum of barytes excited by the λ 2536 radiation of the mercury arc has been studied at a series of eight temperatures ranging from 85° to 923° K., and data furnished regarding the variations in frequency shift and the width of the principal Raman lines. With increasing temperature a definite decrease in frequency shift is observed, the rate of decrease being greater at higher temperatures. While at low temperatures the internal frequencies of the SO_4 ion are clearly split up into distinct components, these tend to coalesce as the temperature is increased. The lattice oscillations are observed to be much more temperature sensitive than the internal oscillations of the SO_4 group. The 89 cm.$^{-1}$ lattice line and the 648 cm.$^{-1}$ internal frequency are comparatively the least affected by temperature variations.

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EFFECT OF DUST AND HAZE ON THE SPECTRAL DISTRIBUTION OF ZENITH-SCATTERED RADIATION

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1. INTRODUCTION

OBSERVATIONS of the light scattered from the zenith sky made with Dobson's photoelectric spectrophotometer at Jackko, Simla, in April and May 1947 showed that there were certain well marked differences in the intensity-ratios I″/I′ and I′/I as measured on clear and hazy days. Here I, I′, I″ are the intensities of the three wavelengths λ (3110 A), λ′ (3300 A) and λ″ (4450 A) respectively, λ being strongly absorbed by the atmospheric ozone, λ′ only slightly and λ″ not at all. Log I″/I′ when plotted against the zenith distance Z of the sun was found to be markedly higher on hazy days than on clear days. It was further noticed that on hazy days, as Z decreased from 90° to 0°, log I″/I′ had first a rapid decrease, but that later, when Z was near about 45°, its value reached a minimum. It again rapidly increased when Z was less than 20°. Calculations of primary molecular scattering showed that the curve should have continued decreasing with Z right down to $Z = 0$. These deviations from the calculated curve became less marked on days with less haze but were evident even on days of apparently very clear skies.

This peculiarity of the variations of zenith sky light for small zenith distances of the sun can naturally be better observed in low latitudes where high suns are frequent. The present paper gives the results of zenith sky observations obtained on a number of hazy and clear days at Simla and Delhi and discusses the origin of the above phenomenon as due to scattering by large particles.

2. OBSERVATIONAL DATA

Dobson's spectrophotometer directly measures the values of log I″/I′ and log I/I′ for the two pairs of wavelengths in the light scattered from the zenith sky. Since the variations of the two quantities with the zenith distance Z of the sun are in opposite directions, for convenience of comparison, the reciprocal quantity log I′/I instead of log I/I′ is used hereafter and the instrumental constants to be added to log I″/I′ and log I′/I are also dropped out.

The skies at Simla (2·45 km. a.s.l.) are generally clear up to the middle of April, but later the duststorms of the North Indian plains frequently raise dust above the height of Simla. Observations were carried out both on clear cloudless days and on days of different degrees of haziness in April and May, 1947. Due to disturbed political conditions in the country, observations at Simla could again be started only in the month of November, 1947. The skies in the winter series of observations were much clearer than in the hot season, but the lowest zenith distance of the sun obtained in the winter series was only 47° as against 13° in the summer.

Fig. 1 gives the plots of log I″/I′ and log I′/I against the zenith distance Z of the sun measured from sunrise to sunset on a few days at Simla.

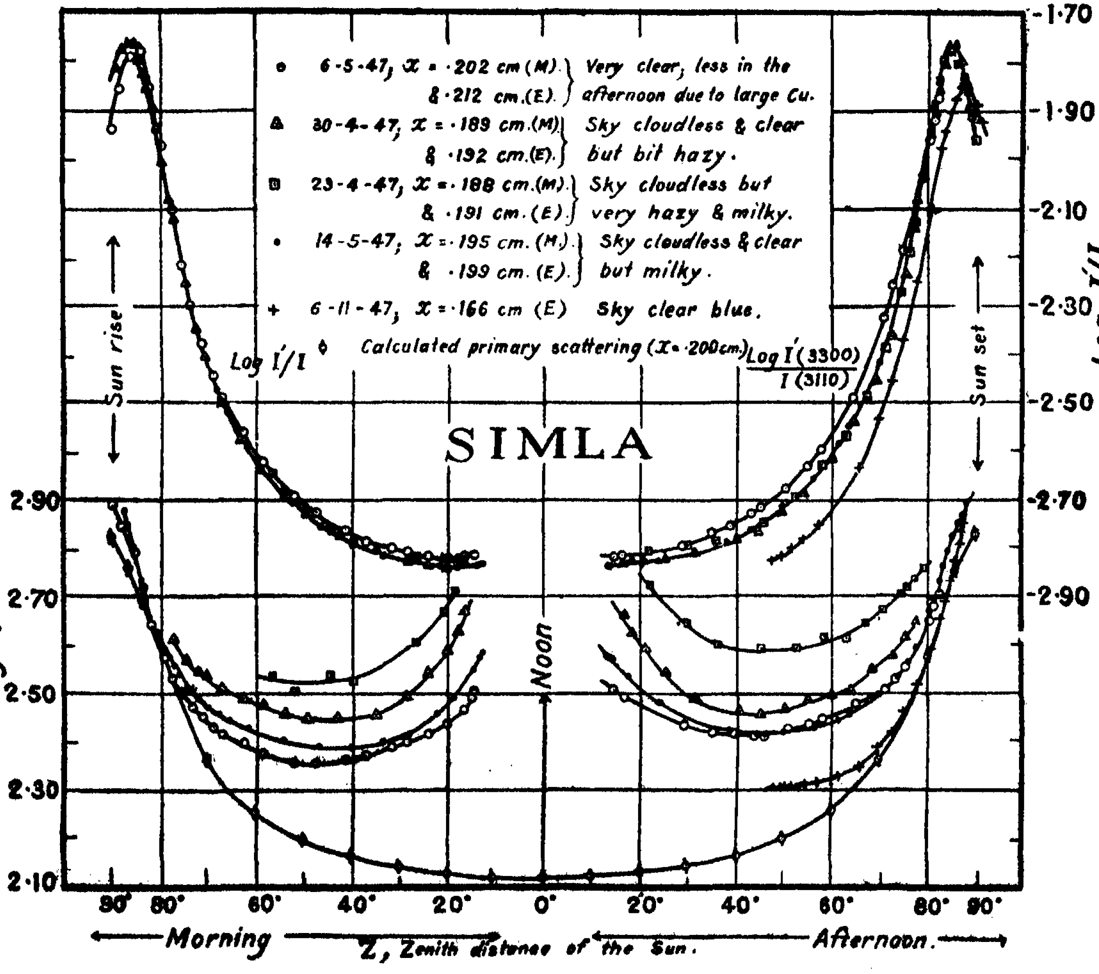

FIG. 1. Observations of zenith sky radiation at Simla

The ozone amounts and sky conditions are also indicated. Fig. 2 gives similar data obtained for Delhi. Though the sky haziness observed at Delhi was much more varied than at Simla, complete curves for Delhi from midday to sunset or sunrise were available on very few occasions. Only the later more complete observations at Simla revealed the usefulness of taking complete series of observations to explain the phenomenon.

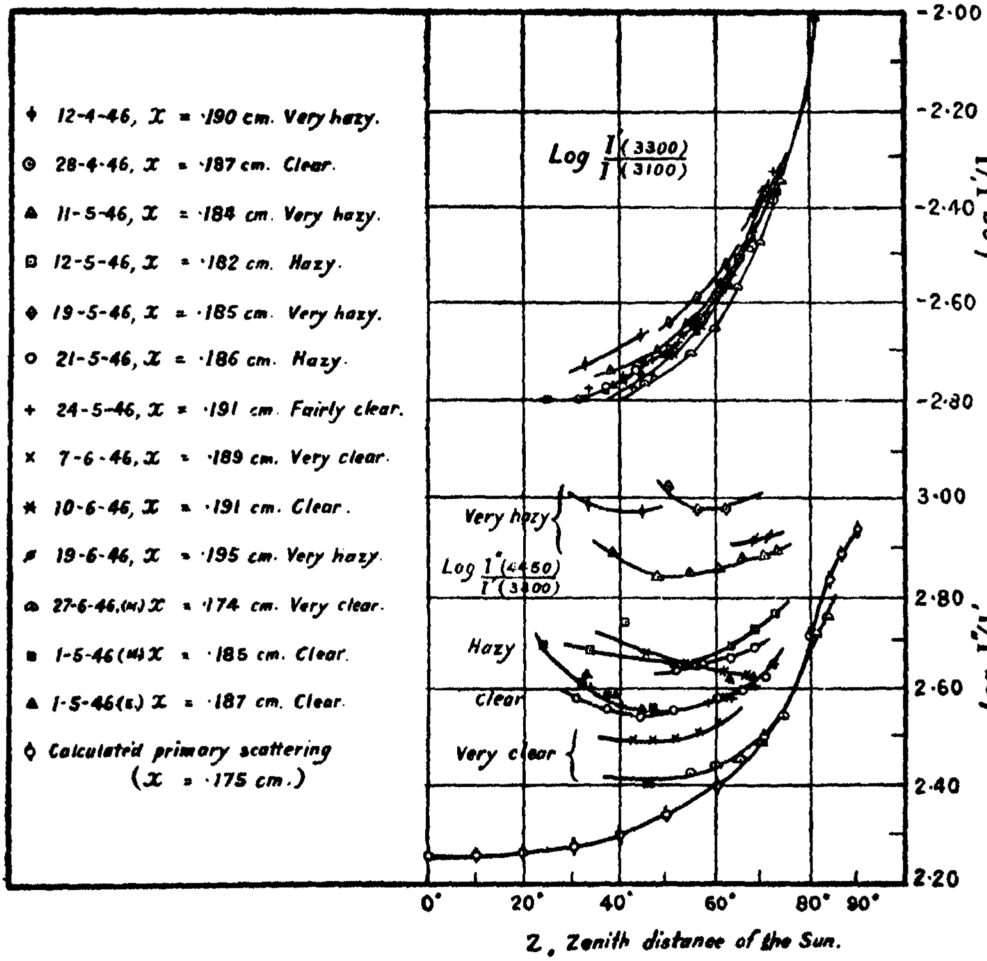

FIG. 2. Observations of zenith sky radiation at Delhi

Calculations were made on the basis of primary molecular scattering alone and curves were drawn showing the amount of light coming from different heights in a pure atmosphere at the wavelengths λ (3110 A), λ' (3300 A) and λ'' (4450 A) corresponding to assumed ozone amounts. The ratios I″/I′ and I′/I for the integrated intensities were calculated from these and these calculated curves are also shown in Figs. 1 and 2.

3. VARIATION OF THE INTENSITY RATIOS WITH THE DEGREE OF HAZINESS OF THE SKY

Since molecular scattering, ozone absorption and particle scattering affect the three wavelengths differently, the two ratios I″/I′ and I′/I would show corresponding differences. Observations show that the ratio for the longer wavelengths is much more susceptible to changes in haziness of the sky than that for the shorter wavelengths. Calculation also shows that changes in log I″/I′ due to the variations in ozone amounts found on the different days of observation are negligible. As the wavelength interval $\lambda''-\lambda'$ between 4450 and 3300 A is much larger than the interval $\lambda'-\lambda$ between 3300 and 3110 A, the effect of haze scattering on log I″/I′ may be expected to be much larger than that on log I′/I.

The upper curves of log I′/I in Figs. 1 and 2 show that (1) with increasing ozone amount, the intensity in the shorter wavelength decreases at all zenith distances and (2) when the ozone amount remains the same but the sky haziness increases, the ratio log I′/I is not appreciably altered at angles of $Z > 45°$ but that at lower angles there is a small but appreciable rise in the curve when the sky is very hazy.

The curves of log I″/I′ show much greater diversity. The lowest curve in the afternoon refers to a very clear day with the least ozone amount 0·166 cm. and the lowest curve in the morning to a clear day with the highest ozone amount 0·202 cm. Higher up there are curves relating to days with nearly the same ozone amount but with different degrees of haziness. It is obvious that sky haze affects the long wavelength curves much more than the ozone amount, increasing haze increasing the relative intensities in the longer wavelength. Thus clearest days in winter show the lowest values of log I″/I′ and very hazy days in the hot season give the highest values; days of intermediate haziness show intermediate values. Since the curves sort themselves out in the order of haziness, the elevation of the curve above the molecular scattering curve at some specified angle—$Z = 45°$ near the minimum is very convenient—can be taken as a measure of the haze.

We can also get a measure of atmospheric haze or turbidity in a different way. It was pointed out in a previous paper[1] discussing 'the effect of dust and haze on direct sun observations made with Dobson's spectrophotometer' that the quantity $\delta'-\delta'' = (L'-L'_0)/m - \alpha'x - (\beta_1'-\beta_1'')$ obtained from direct sun observations would be a convenient measure of atmospheric turbidity. To try this out, the values of log I″/I′ at $Z = 45°$ were plotted against the mean values of $(\delta'-\delta'')$ obtained from direct sun observations made at the same time. Fig. 3 shows these plots separately

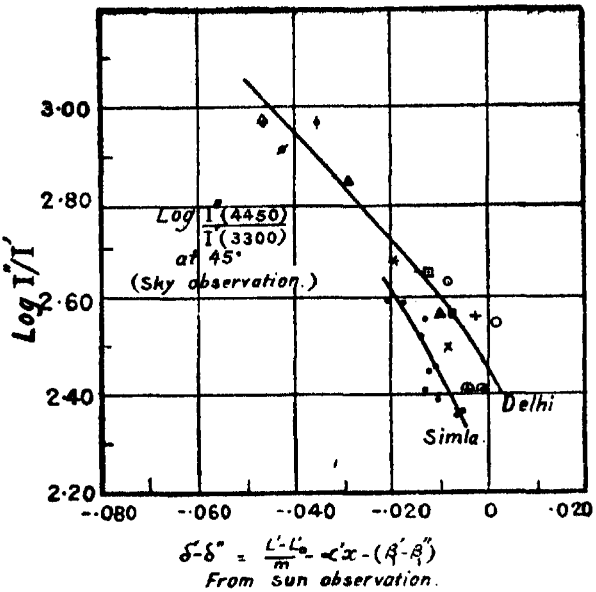

FIG. 3. Atmospheric haze from zenith sky intensity and direct sun observations

for Simla and Delhi. It is seen that log I″/I′ increases more or less regularly with increase in the numerical value of (δ′–δ″). Unfortunately all the observations presented here are those in the summer and the sign of (δ′–δ″) remains negative throughout this period. The numerical value of (δ′–δ″), however, increases with increase in haziness. The observational points for the two places Simla and Delhi show that there is a definite correlation between the value of the ratio log I″/I′ and the amount of haze in the atmosphere. The lateral shift of the Simla curve with respect to the Delhi curve on the side of larger numerical values of (δ′–δ″) is not significant, as the value of the constant to be added to log I″/I′ at the two places is different.

The reason why log I″/I′ increases with increase in the haziness of the sky is obvious. In an ideally clear atmosphere, the scattering is selective and there is predominance of shorter wavelengths in the scattered light, the variation being according to Rayleigh's inverse fourth power law. Any increase of large-sized scattering material in the sky would mean an addition of scattered radiation for which the value of n in the scattering law λ^{-n} would be smaller than 4. The ratio I″/I′ will therefore increase. With increase in the size of the haze particles, the scattered radiation will increase in quantity and become richer in longer wavelengths. For very large particles, however, the scattering becomes non-selective and the ratio I″/I′ would remain practically unaffected.

4. VARIATION OF THE INTENSITY RATIOS WITH THE ZENITH DISTANCE OF THE SUN

Apart from the above-mentioned general increase in the values of $\log I''/I'$ with increase in the haziness of the sky, another very interesting fact is that $\log I''/I'$ shows a minimum near about 45° and a rapid *increase* in value for values of Z less than 20°. The curve of $\log I'/I$ also shows a similar but much feebler rise for low values of Z. Calculations of primary molecular scattering show that the curve should steadily decrease and be horizontal near $Z = 0$. The deviations from the calculated curves become less marked on clear days but are quite evident even on days of apparently very clear skies.

The peculiar rise in the curves of $\log I''/I'$ for values of $Z < 45°$ can perhaps be better understood by decomposing the observed curve into the molecular scattering curve and the curve of residue, *viz.*, the difference between the observed and calculated curves. Fig. 4 shows the observed curves, the calculated curves and the residual curves for two days of different degrees of haziness at Simla. The observed curve can be considered to be the resultant of the molecular scattering curve and the residual curve. This residue curve gives the contribution due to large particle scattering.

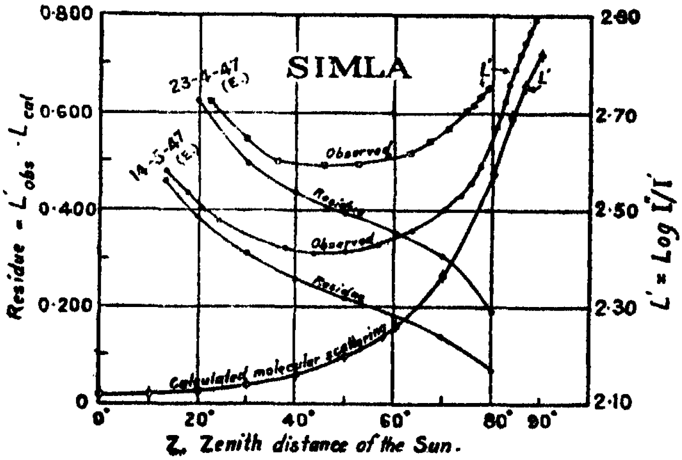

FIG. 4. Resolution of zenith sky intensities into molecular and large particle scattering intensities—at Simla

5. GENERAL REMARKS

It is well known from the work of Mie,[2] Lord Rayleigh,[3] Blumer,[4] Stratton and Houghton,[5] Sinclair[6] and others that the scattering of light by transparent spherical particles which are not small in size compared with the wavelength of light differs from the scattering by small particles in the following important respects.

(1) The scattering cross-section S is a function of $2\pi r/\lambda$. It is very small for values of $2\pi r/\lambda < 0{\cdot}5$ but increases rapidly with increase of $2\pi r/\lambda$, reaching a maximum at a value which depends on the refractive index of the particles, then goes down to a minimum, again reaches a feebler secondary maximum and ultimately reaches a value equal to $2\pi r^2$ for large values of $2\pi r/\lambda$. For particles of refractive index 1·33, the first maximum is reached when $2\pi r/\lambda$ is nearly 6 and the first minimum when it is nearly 11.

(2) A large fraction of the total scattered light by large particles is concentrated in a small cone about the direction of the incident light. The larger the value of r/λ, the smaller is the angle of the cone within which half the total scattered light is concentrated. For example, for wavelengths with $2\pi r/\lambda$ equal to 160, half the light lies within a cone of semi-vertical angle 7°.

The detailed analysis of scattering by atmospheric haze is very complicated, because the atmosphere contains particles of many sizes and the incident light is composed of many wavelengths. Moreover, the particles are not concentrated in a thin layer but are spread out in depth so that secondary and multiple scattering becomes important and detailed calculation becomes exceedingly difficult.

The author wishes to express his grateful thanks to Prof. K. R. Ramanathan for his interest and advice in the present work.

SUMMARY

Observations of the zenith scattered light made with Dobson's photoelectric spectrophotometer at Simla and Delhi showed that the intensity ratio I''/I' for the longer wavelengths when plotted against the zenith distance Z of the sun was found to be markedly higher on hazy days than on clear days. The observed curves sorted themselves out in the order of haziness and the elevation of a curve above the curve calculated on the basis of molecular scattering could be taken as a measure of the haze. $(\delta'-\delta'')$, obtained independently from direct sun observations, was another measure of haze and on plotting these two against each other, it was found that there was clear correlation between them.

Another interesting fact observed was that as Z decreased from 90° to 0°, $\log I''/I'$ had first a rapid decrease, showed a minimum near about 45° and for still lower values of Z showed an *increase*, the increase being rapid below 20°. Calculations of primary molecular scattering showed that the curve should steadily decrease with Z right down to $Z = 0°$. These deviations from the calculated curve became less marked on clear days but were

quite evident even with apparently very clear skies. On decomposing the observed curve into the molecular scattering curve and the curve of residue, it was seen that this residue curve indicated very large intensities at small angles from the direction of incidence, decreasing rapidly as the angle increased and could be reasonably attributed to scattering by large particles present in the atmosphere.

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DIFFRACTION OF LIGHT BY VERY HIGH FREQUENCY ULTRASONIC WAVES: EFFECT OF TILTING THE WAVE FRONT

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1. Introduction

Asymmetry in the diffraction spectra produced by a tilt in the sound wave front from the position of normal incidence was observed by Debye and Sears[1] and by Lucas and Biquard.[2] The diffraction spectrum of the *m*th order attains its maximum intensity for a tilt angle given by

$$\theta = \sin^{-1} m\lambda \,/\, 2\mu_0 \cdot \lambda^*, \tag{1}$$

where μ_0 is the refractive index of the medium, λ is the wave length of light in vacuum and λ^* is the wave length of sound in the medium. Detailed investigations were made later by Bär[3] and Parthasarathy.[4] Photographs obtained by Bar showed the asymmetry introduced on tilting the sound wave front through an angle of $< 1°$. For a truly normal incidence, a symmetrical diffraction picture and for oblique incidence, a picture with more orders on one side than on the other were obtained. Parthasarathy used progressive sound waves set up in a 12″ column of benzene at a frequency of 7·37 Mcs/sec. and measured the tilt angles in a rough way by attaching a rigid steel rod of 31 cm. to the crystal holder and observing the readings of its end on a vertical scale. Tilting the sound wave front from the normal incidence position, greatest asymmetry in the diffraction spectrum was noticed at an angle of 22′. When the angle of incidence was further increased, the number of diffraction images was found to decrease, and finally disappear almost completely at about 2°. Using a frequency of 20 Mcs./sec., Parthasarathy[5] later showed that intense diffraction spectra on one side of the central image could be obtained for certain angles of incidence given by the Bragg relation. Rytov[6] investigated the effect of tilting the sound wave front on diffraction, both theoretically and experimentally, in the range of 30 to 70 Mcs. His observations showed that at these frequencies, the intensity distribution approximated closely to selective reflection at the Bragg glancing angle. Quantitative measurements of the intensity of first order diffracted light in air for varying angles of incidence were made by Korff.[7] The ratios of the intensities of the first order to the central order were estimated on a microphotometer and compared with the theory of Brillouin. A maximum of diffracted light was found at the Bragg angle of incidence.

The highest frequency at which diffraction effect has so far been studied is thus only 70 Mcs./sec. and this was by Rytov. During the past few years, we have been studying the different aspects of diffraction by very high frequency ultrasonic waves and we have succeeded in generating and using sound waves of frequencies upto 200 Mcs./sec. for this purpose. In this investigation, the effects produced by tilting the wave front are described in some detail.

2. EXPERIMENTAL DETAILS

Four different frequencies, namely, 25, 50·36, 102·6 and 177·2 Mcs./sec. have been used. The wave-length of sound in water corresponding to the highest frequency used here is 0·000849 cm. This is only about 14 times the wave-length of sodium yellow light, which is generally employed by us for obtaining the patterns. The oscillators for generating the 177·2 and 102·6 Mcs. radio waves are specially designed and constructed using a T-55 valve. The circuit for the 50 Mcs. oscillator is the same as that used for 100 Mcs. with slight modifications. A coil of 2″ diameter containing two turns of thick tinned copper wire serves as the tank circuit inductance. A Meissner R. F. choke of 2·5 mH with a current carrying capacity of 250 mA is used in the plate circuit. The crystal is connected to a coil of about four turns of copper wire mounted on an amphenol insulator. By varying the distance of this coil from the tank coil of the oscillator the power input to the crystal can be altered. The 25 Mcs. oscillator is of the regular Hartley type using 815 valve and is also coupled to the crystal by a mutual inductance coil, again enabling us to vary the power of excitation of the crystal.

The arrangement for observing and recording the diffraction patterns is the usual one with slight modifications. Water is the medium in which all the effects described in this paper have been studied and 6 mm. square apertures are introduced in the light emerging from the collimator to get uniform light intensity with square cross-section. Except for the low frequency of 25 Mcs., for all the other frequencies a 3″ glass cell is found to be sufficient for producing progressive waves, the absorption coefficient then being sufficiently high that the wave gets completely damped before touching the bottom of the cell. For the 25 Mcs. ultrasonic wave, however, a 12″ height of glass cell stuffed with glass wool and felt padding at the bottom is used for getting a truly progressive sound wave. Any deviation from the truly progressive nature of the wave can be detected by tilting the cell in a plane at right angles to the direction of the light beam. If any change in the intensity of the diffracted light is noticed it can be taken as an indication that the wave is not a pure progressive wave. This test is necessary and must be applied only when the light beam is incident normally on the faces of the glass cell.

A mirror is rigidly attached to the crystal holder and a telescope and scale placed at a distance of about one metre are used to note the position of the crystal holder. The direction of observation through the telescope is set almost parallel to the direction of the light beam. With this arrangement, very slight variations in the tilting of the crystal holder can be easily detected.

3. RESULTS

Starting from the normal incidence position of the sound wave front, the crystal holder is tilted through known angles and the intensities of both the first order diffraction lines are visually estimated. For all the four frequencies of the sound waves, the maximum intensity of the first order diffraction line is adjusted to be approximately the same and the effect of tilt studied. Visual estimates of the intensities of + 1 and − 1 orders for different angles of tilt θ from the normal incidence position are given in Table I. Table II gives the angles through which the crystal has to be tilted

TABLE I

25 Mcs. ..	θ	−18′	−11·5′	−6′	−4·5′	0	4·5′	6′	11·5′	18′		
	I_{+1}	0	0	0	0	3	8	10	20	12		
	I_{-1}	12	20	10	8	3	0	0	0	0		
50·36 Mcs. ..	θ	−32′	−26′	−21′	−16′	−3′	0	3′	16′	21′	26′	32′
	I_{+1}	0	0	0	0	0	1	1·5	6	10	20	8
	I_{-1}	8	20	10	4	1·5	1	0	0	0	0	0
100·26 Mcs. ..	θ	−56′	−52′	−50′	−46′	−43′	0	43′	46′	50′	52′	56′
	I_{+1}	0	0	0	0	0	0	2	4	10	20	4
	I_{-1}	4	20	10	4	2	0	0	0	0	0	0
177·2 Mcs. ..	θ	−89′	−88′	−84′	0	84′	88′	89′				
	I_{+1}	0	0	0	0	1	10	20				
	I_{-1}	20	10	1	0	0	0	0				

TABLE II

Frequency of sound in Mcs./sec.	θ Calculated	θ Measured
25	12·7′	11·5′
50·36 (+1)	25·5′	26′
50·36 (+2)	51′	52′
102·6	51·4′	52′
177·2	90′	89′

from the normal incidence position to get a maximum intensity for the first order. This angle is compared with the angles computed from formula (1). With increased power input, even the second order at 50 Mcs. could be obtained, but only at the proper inclination and the observed angle compared well with that calculated from the formula. In Table III, the value given in the columns designated by $\phi\frac{1}{3}$ and $\phi\frac{1}{2}$ represents the fraction, with reference to the Bragg reflection angle in each case, of the sound wave front tilt from the maximum intensity position required to reduce its intensity to $\frac{1}{2}$ and $\frac{1}{3}$ respectively. ϕ_0 stands for the tilt angle, similarly expressed as a fraction, at which the disappearance of the order takes place. This table brings out the increasing sharpness of the phenomenon with increasing frequency of sound waves.

TABLE III

	25	50	102	177 Mcs.
$\phi_{1/2}$ ..	1/2	1/5	1/26	1/90
$\phi_{1/3}$ ..	2/3	1/3	1/13	1/50
ϕ_0 ..	4/3	9/8	1/4	1/11

The estimates of intensities are plotted in Fig. 1. For the lower frequencies of 25 and 50 Mcs., both I_{+1} and I_{-1} are plotted, while for the two higher frequencies, only I_{+1} is given.

The special features observed in the case of very high frequencies are summarised below.

(*a*) It has not been possible to get the second or higher orders in the diffraction patterns. This is in sharp contrast with the observations at low frequencies where the second and higher orders are easily excited with moderate power.

(*b*) The first order diffraction line appears with maximum intensity not for normal incidence but when the light rays meet the sound wave front at the Bragg angle of reflection. In this position, only a single diffraction line on the appropriate side is obtained, the diffraction line on the other side of the central image having completely disappeared. In no position has it been possible to get both the first order lines on either side of the centre at the same time.

(*c*) The value of the angle for which the first order line attains its maximum intensity is quite critical. Fig. 1 shows that a slight tilt of the crystal holder, about 2′ for the 102 Mcs. and 1′ for the 177 Mcs., will reduce the intensity of the diffraction order by half. Contrary to this, the behaviour of diffraction at 50 and 25 Mcs. shows that in this region the range of reflection is not sharp. Tilting the crystal by 13 for the 100 Mcs. and 8′ for the

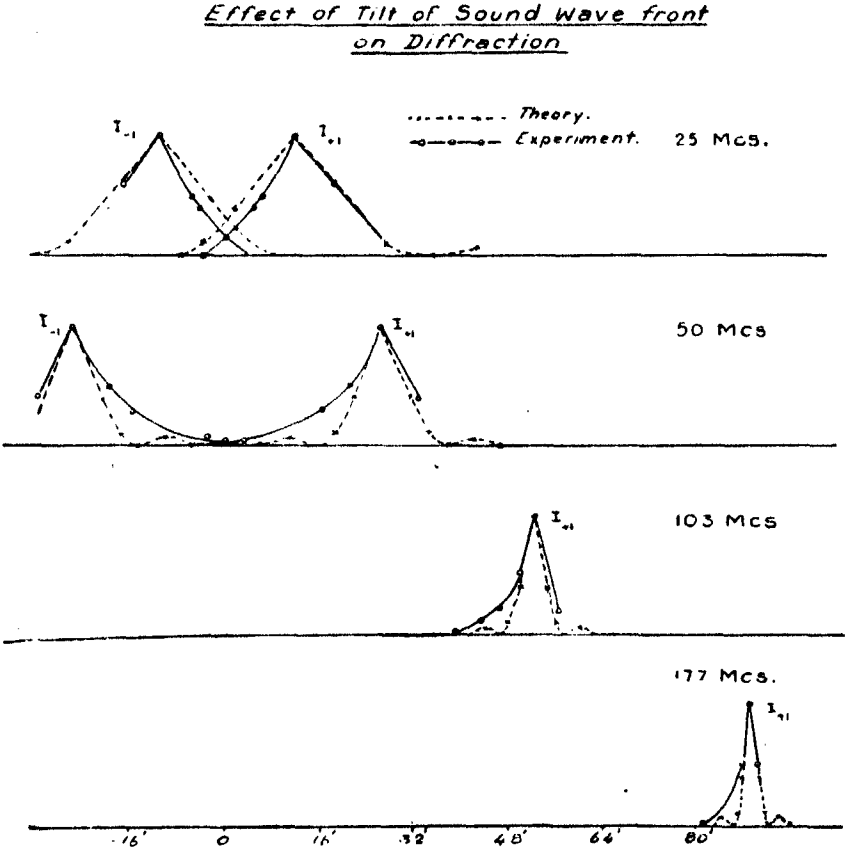

Fig. 1

177 Mcs. from the maximum intensity position of the first order, makes the diffraction effect completely disappear. Thus for normal incidence, no diffraction lines are obtained at these frequencies whereas for 25 and 50 Mcs., at normal incidence the first order lines on both the sides of the central image are obtained symmetrically though with less intensity. The disappearance of diffraction for normal incidence for the very high frequencies shows that the diffraction of light in the ordinary sense does not exist in this region. On the other hand, the reflection phenomenon predicted by Brillouin becomes conspicuous.

4. COMPARISON WITH THEORY

Raman and Nath[8] have given a generalised theory of diffraction in which was obtained a difference-differential equation whose solutions correspond to the amplitudes of the diffraction orders. Nath[9] has solved the difference-differential equation by the series method and has shown that the maxima of intensity of first and second orders of diffraction occur at angles of $\lambda/2\mu_0\lambda^*$ and $\lambda/\mu_0\lambda^*$ under certain conditions. This result is in agreement with our observations. An attempt to calculate the intensities using the expressions given by Nath with suitable parameters has not been successful as it is found that the series is not convergent. In the same paper Nath has suggested a method of determining the amplitude of the fluctuation of the refractive index at high supersonic frequencies by determining the ratio of the intensities of central to the first order for normal incidence and + 1 to − 1 order for oblique incidence. Such observations are not possible at the very high frequencies used by us since both the diffraction orders are never present at the same time.

Following the procedure adopted by Brillouin, expressions for intensities of first and second orders of diffraction have been deduced by David,[10] on the assumption that the higher orders are of negligible intensity. To a first approximation the following expression is obtained for I_{+1}, the fraction of the intensity of the first order to the total incident light.

$$I_{+1} = \left(\delta \frac{\sin\left(\alpha - \frac{1}{2}\right)\bar{x}_0}{\left(\alpha - \frac{1}{2}\right)}\right)^2 \tag{2}$$

where $\delta = \mu\mu_0\, \lambda^{*2}/\lambda^2$

$\alpha = \mu_0\lambda^*\theta/\lambda$

and $\bar{x}_0 = \pi\lambda L/\mu_0\lambda^{*2}$.

L is the length of the sound field traversed by light and θ is the inclination of the sound wave front. It can be easily seen that this expression attains its maximum intensity when $\alpha = \frac{1}{2}$ or $\theta = \lambda/2\mu_0\lambda^*$. This result is the same as (1) and is in agreement with the experimental observations. The maximum value of I_{+1} denoted by I_m comes out as

$$\begin{aligned} I_m &= \delta^2\bar{x}_0^2 \\ &= \frac{\pi^2\mu^2L^2}{\lambda^2} = \frac{1}{4}\left(\frac{2\pi\mu L}{\lambda}\right)^2 \end{aligned} \tag{3}$$

Using I_m given by equation (3), we get the expression (2) modified as

$$I_{+1} = I_m\left(\frac{\sin\left(\alpha - \frac{1}{2}\right)\bar{x}_0}{\left(\alpha - \frac{1}{2}\right)\bar{x}_0}\right)^2. \tag{4}$$

Substituting

$$\theta = \frac{\lambda}{2\mu_0\lambda^*} + \phi,$$

where ϕ is the deviation of the sound wave front from the maximum intensity position of the first order, we get

$$\bar{x}_0\left(a-\tfrac{1}{2}\right)=\frac{\pi L\phi}{\lambda^*}.$$

The expression for the intensity of the first order becomes

$$I_{+1}=I_m\left(\frac{\sin\frac{\pi L\phi}{\lambda^*}}{\frac{\pi L\phi}{\lambda^*}}\right)^2. \tag{5}$$

This relation is extremely important and contains many noteworthy features which are supported by experiment. These features are described below in some detail. The intensity of a particular order will vanish whenever $L\phi/\lambda^*$ is an integer other than zero. Thus, there are three ways of making a diffraction line periodically vanish. The first is by making the tilt angle ϕ of the sound wave front take successively the values λ^*/L, $2\lambda^*/L$ and so on. This phenomenon was experimentally observed by Debye and Sears and a simple explanation was given by Raman and Nath. The second is by making the sound field length L take successively the values λ^*/ϕ, $2\lambda^*/\phi$ and so on. This phenomenon has not been cbserved so far by any of the investigators. Korff[7] studied the dependence of intensity on the length of the sound field but his results show only a tendency towards decreasing intensity with increasing length at a certain stage but do not show a passage through successive minima. Such a passage through successive minima has been observed by us using a specially large-sized crystal and results which are in agreement with the above theory obtained. These will be described in a separate communication. The third method is to make λ^* take successively the values $L\phi$, $L\phi/2$ and so on. No one appears to have worked on these lines. For normal incidence, ϕ in respect of the first order line is equal to θ given by (1) with $m = 1$ and substituting this value in (5), we have

$$I_{+1}=I_m\left(\frac{\sin\frac{\pi L\lambda}{2\mu_0\lambda^{*2}}}{\frac{\pi L\lambda}{2\mu_0\lambda^{*2}}}\right)^2.$$

As the numerator in the bracket is always less than 1, we cannot have even the first order line appearing with appreciable intensity in normal incidence if $\pi L\lambda/2\mu_0\lambda^{*2}>>1$. This is equivalent to saying that no diffraction patterns will be observed in normal incidence if $\lambda>>\lambda^{*2}$ because $\pi L/2\mu_0$ is generally of the order of unity. At 100 Mcs., λ^{*2} is 225×10^{-8} and λ is already about 25 times and therefore intense diffraction patterns cannot appear in normal incidence. For higher frequencies, it is still worse and these conclusions are well supported by our observations. It can be easily seen by differentiating (5) that the sharpness of diffraction depends only on the value of $\pi L/\lambda^*$. That is to say, for very high frequencies and large lengths of the sound field, the phenomenon resembles reflection more than diffraction. The sharpness of diffraction does not depend on any other factor like the intensity of the sound field. These conclusions are entirely in conformity with our observations. Using the expression (5), the value of I_{+1}/I_m is calculated for all the four frequencies used and is given in Table IV for a length of sound field of 1 cm. which is the size of the crystal used by us. The intensities are plotted in Fig. 1 keeping I_m constant for all the frequencies. Experimental curves fit extremely well with the theoretical curves. The only point in respect of which there is a discrepancy relates to the gradual fall in intensity as seen in the experimental curves, whereas the theoretical curves show small subsidiary maxima. This is probably due to the fact that the sound field is not the ideal one with undamped amplitude as has been assumed in the theory.

TABLE IV

I_{+1}/I_m	ϕ (177 Mcs)	ϕ102 (Mcs.)	ϕ (50 Mcs.)	ϕ (25 Mcs.)
1	0	0	0	0
·41	1·5′	2·5′	5·1′	10·4′
·09	2·2′	3·8′	7·7′	15·5′
0	2·9′	5·0′	10·3′	20·7′
·045	4·4′	7·5′	15·4′	31′
0	5·8′	10′	20·6′	41·4′
·016	7·3′	12·5′	25·7′	51·3′

It is also seen from equation (5) that the maximum intensity of the first order obtained by tilting the wave front to the appropriate reflection angle is independent of the frequency of the sound wave and is only a function of μ, L and λ.

5. SUMMARY

Diffraction of light by ultrasonic waves of frequencies 25, 50·36, 102·6 and 177·2 Mcs. set up in water has been studied with particular reference to the effect of tilting the wave front. Certain special features which are characteristic of the very high frequencies employed have been observed. The following are the important amongst them. In contrast with the observations at low frequencies, the first order diffraction is predominant at moderately high frequencies like 50 Mcs. and all the higher orders are suppressed. At 100 Mcs. and above, even the first order lines do not appear for normal incidence but when the sound wave front is tilted from this position to the appropriate side by an angle equal to the Bragg reflection angle, the corresponding order makes its appearance with maximum intensity. At these high frequencies, in no position has it been possible to get both the first order lines on either side of the centre at the same time. For very high frequencies and large lengths of the sound field, the angular range during which a particular diffraction line appears is found to be extremely sharp and narrow. With increasing frequency, the sharpness is found to increase. Experimental observations regarding this sharpness of range are made and compared with the result obtained out of an expression derived from the work of David and Brillouin. The agreement is very satisfactory.

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STUDIES IN ATMOSPHERIC OZONE

Part II. Daily Measurements of Atmospheric Ozone and of (δ'-δ''), a Measure of Atmospheric Turbidity, at Delhi

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§1. INTRODUCTION

THE greater part of our knowledge of atmospheric ozone has come from spectrophotometric measurements of solar radiation in the Hartley absorption band in the near ultra-violet. Starting from the work of Fabry and Buisson,[1] Dobson and co-workers[2] have improved and simplified the methods of observation and made extensive surveys of atmospheric ozone including its general distribution over the earth,[3, 4, 5] the dependence of the total ozone amount on meteorological conditions in Europe,[5, 6, 7] and its distribution in the vertical.[8, 9] Recently, Dr. Dobson[10] with Drs. Brewer and Cwilong has summarised the present position regarding the role of ozone in meteorology.

Measurements of atmospheric ozone in low latitudes are few. For one year in 1929, measurements were made at the Solar Physics Observatory, Kodaikanal[3] with Dobson's photographic photometer, forming part of Dobson's world-wide survey of atmospheric ozone. A further study was made by Dr. Chiplonkar[11] at Bombay during the period 1936–38 using the same photographic instrument. He found general agreement with the Kodaikanal results in respect of seasonal variation, but could find no correlation between the daily values of ozone and surface meteorological conditions.

The most convenient instrument for measuring atmospheric ozone is Dobson's photo-electric spectrophotometer.[12, 13] The photo-electric instrument has great advantages over the photographic one, owing to its greater sensitivity, accuracy and ease of measurement. The instrument is sufficiently sensitive for measurements to be made of the light scattered by the zenith sky even when the sun is slightly below the horizon. This enables the vertical distribution of ozone to be investigated. One of the instruments was acquired in 1940 by the India Meteorological Department. The instrument was set up and preliminary measurements were made by

Dr. Ramanathan and co-workers,* but war-time work prevented the continuation of the work. The present writer began to work with the instrument in 1945.

In view of the fact that during the winter and the following dry season, western disturbances regularly travel across North India, it was considered desirable to take regular observations at Delhi for at least a year. Daily observations were accordingly commenced at Delhi in November 1945 and the results of measurements of the atmospheric ozone during the period November 1945 to March 1947 are discussed in this paper. The effects of dust and haze on ozone measurements came up prominently for attention in the course of the observations at Delhi and this has been discussed in another paper.[14]

§2. BRIEF DESCRIPTION OF THE INSTRUMENT AND THE METHOD OF CALCULATING THE OZONE AMOUNT

The instrument consists of a quartz monochromater for isolating the wavelengths 3110 A and 3300 A and a photo-electric cell and amplifier for measuring their relative intensities. The light of the two wavelengths is made to fall on the photo-electric cell one after the other, a rotating shutter admitting one wavelength in two opposite quarters of a rotation and the other wavelength in the other two quarters. By means of a calibrated optical wedge, the light of the wavelength which produces the greater photo-electric current can be cut down so that there are no jumps in current when light of one wavelength is replaced by that of the other. The thickness of the optical wedge in that condition gives a measure of the relative intensities of the two lines. In order to get an estimate of the difference in intensities caused by the difference in scattering at the two wavelengths by air molecules, and by dust, particles of ice or water, measurement is also made of the ratio of intensities of 3300 A and 4450 A (a wavelength well outside the ozone absorption band). By calculation from this, the relative loss of intensity due to scattering at 3300 A and 3110 A is determined and allowed for. The zenith distance of the sun is obtained from the time of observation, using a chart similar to the one described by Dr. Karle Schütte in *Meteorologische Zeitschrift*, 1931. Both the airmass m and the path length μ through the ozone region, each expressed in terms of its normal thickness, are obtained from the zenith distance. For calculating μ, the curves supplied with the instrument, which assumed the mean height of ozone to be 22 km., have been used. According to the later analysis made in another paper,[15] it is found that the mean height of ozone over Delhi is 25–27 km. This difference in mean height from the assumed height of 22 km. causes an error in the calculated value of the ozone amount x of about $0{\cdot}1\%$ at $Z = 50°$, $0{\cdot}2\%$ at $Z = 60°$, $0{\cdot}5\%$ at $Z = 70°$ and $1{\cdot}2\%$ at $Z = 76°$. Only observations with $Z < 70°$ were used in the calculation of daily ozone amounts.

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The total amount of ozone x is calculated by the equation,

$$x = \frac{(L_0 - L) - K'(L' - L'_0) - m\{(\beta_1 - \beta'_1) - K'(\beta'_1 - \beta''_1)\}}{\mu\{(\alpha - \alpha') - K'\alpha'\}} \tag{1}$$

where $L = \log I/I'$, $L_0 = \log I_0/I_0'$, $L' = \log I''/I'$, $L'_0 = \log I_0''/I_0'$,

I, I', I'' being the intensities of the three wavelengths 3110, 3300 and 4450 A received by the instrument and I_0, I_0', I_0'' the corresponding intensities outside the atmosphere; β_1, β_1', β_1'' the coefficients of attenuation due to Rayleigh scattering; α, α', α'' the absorption coefficients per cm. of ozone at N.T.P. for the three wavelengths; $K' = (\delta - \delta')/(\delta' - \delta'')$ where δ, δ', δ'' are the coefficients of attenuation due to non-molecular particle scattering, it being assumed that δ is proportional to λ^{-n} where n has the value $1{\cdot}3$.

The above formula differs from the one used by Dobson in that the allowance for non-molecular scattering has been made somewhat differently. The question has been fully discussed in a separate paper.[14] The change makes very little difference in the calculated ozone amounts on days with clear skies.

In 1941, Dobson[16] suggested the following revised formula for calculating ozone amounts from direct sun observations:

$$x = \frac{(L_0 - L)}{(\alpha - \alpha')\mu} - \frac{(\beta_1 - \beta'_1)\,m}{(\alpha - \alpha')\,\mu}. \tag{2}$$

If m is small, $m/\mu \approx 1$ and the value of the second term on the right hand side of the equation according to the values of the constants given by Dobson is $0{\cdot}085$ and is assumed to hold on clear days. The value is increased to $0{\cdot}095$ on hazy days and even to $0{\cdot}105$ on very hazy days. Tonsberg and Olsen[17] in their work at Tromsø, used the following single formula as suggested by Dobson.[16]

$$x = (L_0 - L)/1{\cdot}17\,\mu - 0{\cdot}085 \tag{3}$$

For comparison, the values calculated according to equations (1), (2) and (3) are given in different columns under x, $x_{D'}$ and x_D respectively in the Appendix. For x and $x_{D'}$, the values of the constants assumed for Delhi and given in the Appendix were used, and the deviation of m/μ from unity at different zenith distances of the sun was also taken into account. For

x_D, equation (3) was used as it is. On clear days, the two formulæ for x and $x_{D'}$ give practically the same values, but on hazy days there are significant differences of opposite signs in the winter and hot seasons respectively. x_D is generally higher than $x_{D'}$ by 0·003 cm.

§3. RECALIBRATION OF THE OPTICAL WEDGES

When work with the instrument was resumed in 1945 at Delhi, the first step taken was to redetermine the values of the constants L_0 and L_0' by extrapolating from the observed values of L and L′ on clear days against the ozone paths at different zenith distances of the sun. The values of L and L′ and of μ were obtained from charts supplied with the instrument. It was found that even on very clear days such plots showed some systematic deviations from the expected straight lines. For calibrating the instrument, the method suggested by Dr. Dobson[18] was employed. The instrument was set so as to pass light of wavelength 3300 A into the photoelectric cell. In that condition, the deflection of the galvanometer was a measure of the intensity of light of this wavelength falling on the photo cell. The wedge was set at some known reading near its thin end and the sensitivity of the instrument adjusted so as to give a convenient deflection in the galvanometer. A thin metal gauze of known transmission ratio was then placed in the path of the beam of light causing a decrease in the deflection of the galvanometer. The gauze was now removed and the same decrease of deflection produced by moving the wedge. The difference between the two wedge readings corresponds to the attenuation caused by the perforated metal gauze.

Some details regarding the calibration may be recorded. The mercury ultra-violet lamp supplied with the instrument was not found to give sufficient light to enable satisfactory readings to be taken in the thicker parts of the wedge. Sunlight on very clear days of settled weather between 10 hours and 14 hours was therefore used for the calibration. A machine-perforated zinc gauze of suitable mesh, blackened chemically with silver nitrate, was used to attenuate the incident sunlight. This was placed immediately in front of the prism of the sun-director and kept moving in its own plane so as to average out non-uniformities due to the finite number and spacing of the holes. Steady deflections were obtained and individual readings could be repeated to within 1°. The mean differences ΔD between the dial readings, with and without the gauze, were determined throughout the range and these were plotted against the mean dial readings (Fig. 1). On the same diagram is also shown the curve that would have been obtained if the calibration chart supplied with the instrument were correct. The observations

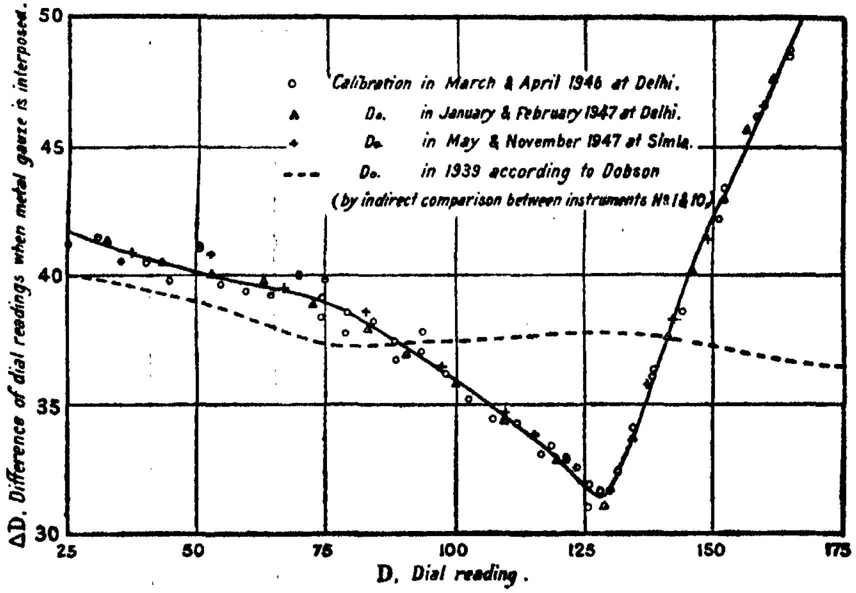

FIG. 1. Calibration of optical wedges in Dobson's ozone spectrophotometer (No. 10) using perforated zinc gauze

were repeated on many clear days in the months of March and April 1946, with different dial readings as starting points. Similar detailed calibration was again done in January and February 1947 at Delhi and in May and November 1947 at Simla. The results are all plotted on the same diagram and show the constancy of the new calibration. Considering that the instrument had been in Delhi throughout the hot summer with temperatures as high as 115° F·, this is a satisfactory result. The mean transmission ratio of the gauze was determined to be 41·05%, the corresponding value of ΔL being 0·387.

From the smooth curve of Fig. 1, ΔL/ΔD was calculated for each degree of the dial and with the addition of a suitable constant, the calibration curve of L against D was obtained by taking successive differences. Fig. 2 shows both the old and new calibration curves, the two being made to coincide at 90°. There is increasing deviation between the two curves on either side of 90°, but on the thicker side of the wedges, the curves close up again after 140°. Tables giving log I/I′ for every 0°·1 of the dial were prepared for routine use.

For a number of clear days on which a large number of observations for all heights of the sun were available, L and L′ were plotted against μ. The new chart gave a definitely better straight-line fit of the observations.

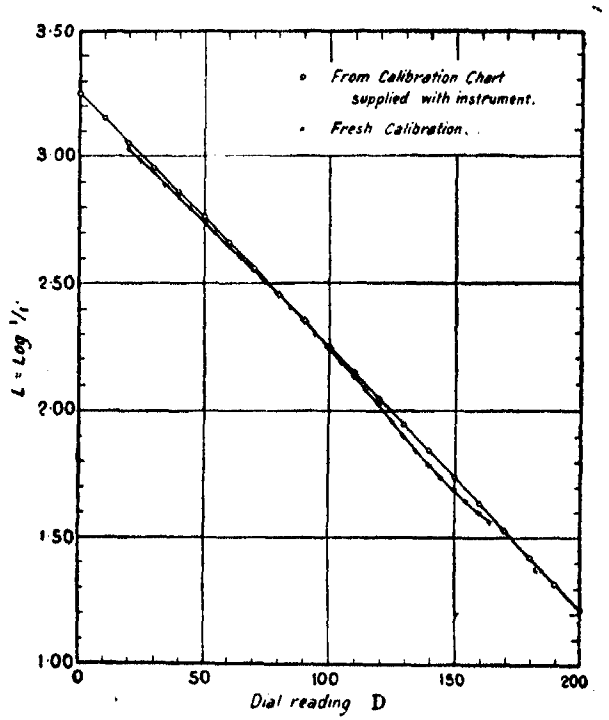

FIG. 2. Old and new calibration curves of optical wedges

As an example, in Fig. 3, the observations on 18–4–1946 are compared with the two calibrations. There is, however, a tendency for the values of L at high values of μ to lie out. This is to be attributed to the incorrectness of the assumption that 22 km. is the mean height of the ozone layer. According to the analysis made in another paper[15] the mean height in India is 25–27 km.

It is now understood from Dr. Dobson[18] that " when the whole batch of new ozone instruments was calibrated, the wedge in the original instrument (No. 1) only was calibrated directly by the detailed method described above; each of the new instruments was calibrated only by comparing with instrument No. 1, simultaneous observations being taken at all heights of the sun with the two instruments. This method was quicker and it was expected that the results of all instruments would be exactly comparable ". In view of the experience with instrument No. 10, it seems desirable to calibrate each instrument individually with a sufficiently intense source of ultraviolet radiation. In India, with the high noon-day sun, advantage can be taken of clear days for the calibration.

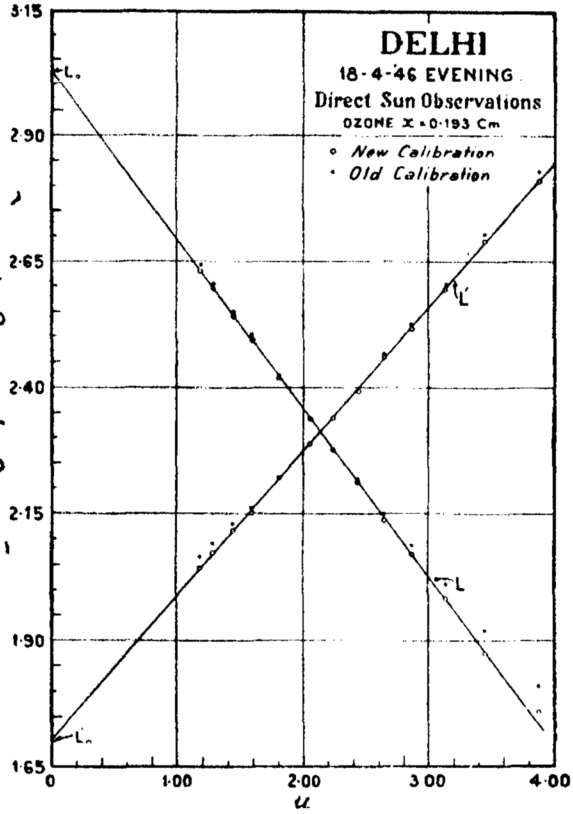

FIG. 3. Use of old and new calibration curves to determine the constants L_0 and L_0'

§4. DETERMINATION OF THE CONSTANTS L_0 AND L_0' FOR THE INSTRUMENT

L_0 and L_0' correspond to the ratios of the intensities of 3110 A and 3300 A, and of 4450 A and 3300 A outside the atmosphere. To obtain these, the values of L and L′ obtained on a number of clear days with all heights of the sun were plotted against corresponding values of μ, and the values for $\mu = 0$ were obtained by extrapolation. The values of μ for different zenith-distances were taken from the chart supplied with the instrument, and this corresponds to 22 km. for the mean height of the ozone layer. Even if the mean ozone height over Delhi differs somewhat from 22 km., no appreciable error in the determination of L_0 and L_0' will be caused if values of μ greater than 3·5 or 4 are not taken into consideration for the extrapolation. The mean of 60 such determinations on clear days gave $L_0 = 3·020$ and $L_0' = 1·715$, the extreme values of L_0 being 3·004 and 3·033 and those of L_0' 1·700 and 1·733. Individual days' values show a random scatter and o regular drift.

It is interesting to note that no appreciable changes in the values of L_0 and L'_0 were observed in the months of February and March 1946, when large sunspots were reported. On the other hand, haze caused appreciable disturbance in the course of the values of L and L′ as will be seen from Fig. 4 which relates to a very hazy day (17–11–1945).

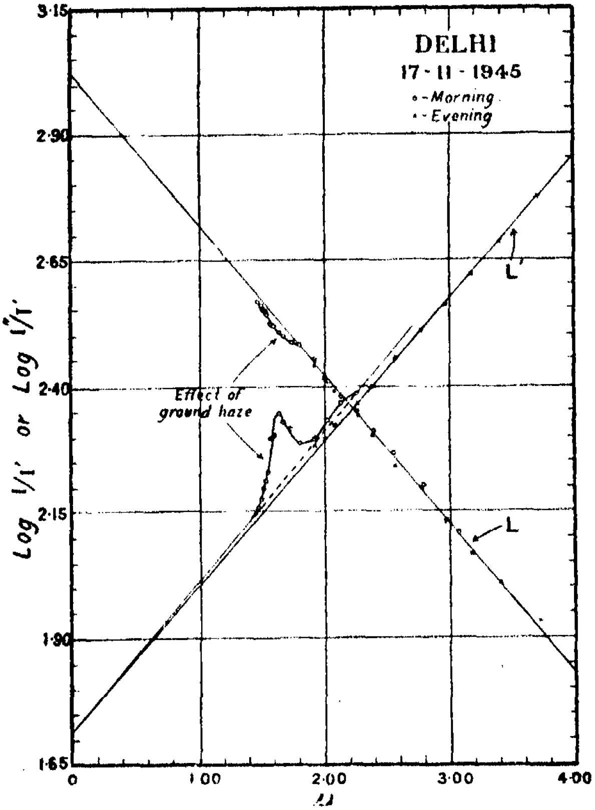

FIG. 4. Direct sun observations on a very hazy day

§5. DIURNAL VARIATION OF ATMOSPHERIC OZONE

Observations with direct sunlight made at different times of the day show a small systematic daily variation of ozone amount. Fig. 5 *a* shows the variation on six consecutive clear days in September 1946; Fig. 5 *b* shows similar curves for a few days in other months. The afternoon values in all instances are higher than the morning ones; there is also a marked dip at about local noon. This dip at noon is not of instrumental origin since the calibration of the wedges had been carefully checked and also the observations with high sun could be obtained without ambiguity.

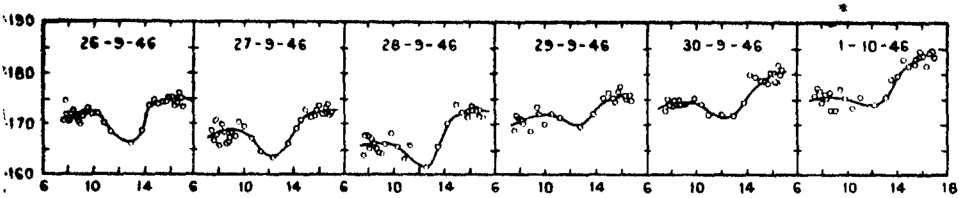

FIG. 5a.

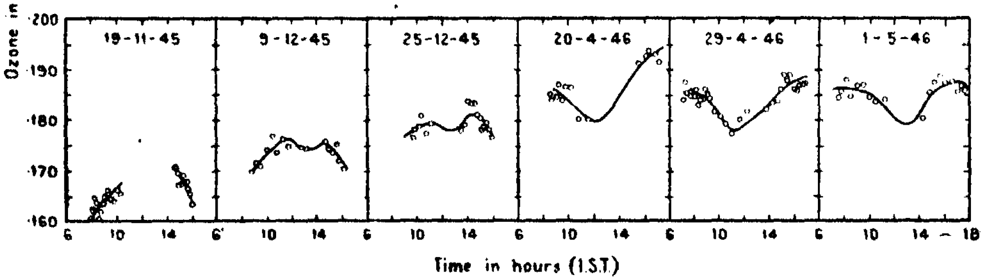

FIG. 5b.

FIG. 5. Diurnal variation of atmospheric ozone

Fig. 6 shows the mean morning and afternoon values of ozone for a number of days on which observations were taken both in the morning and in the afternoon. In almost all cases, the afternoon values were higher than the morning ones.

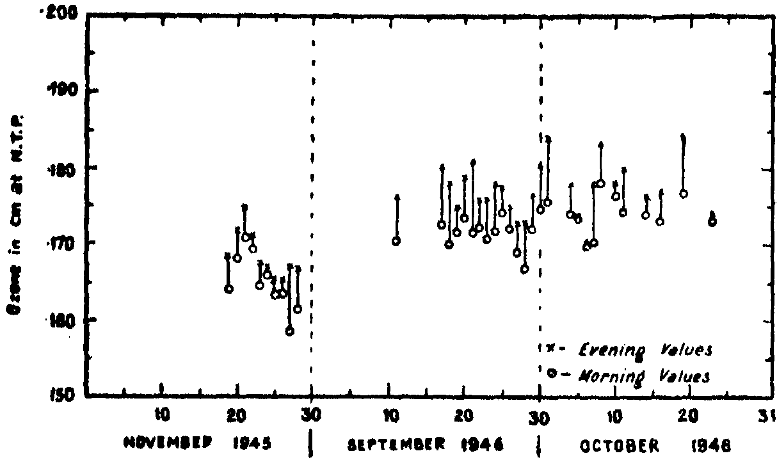

FIG. 6. Morning and evening values of atmospheric ozone on a number of days

There are, however, instances when the morning values were higher than the afternoon ones. Such days were rare and generally occurred when the daily ozone amounts were falling. Fig. 7 gives the results for a few such consecutive days.

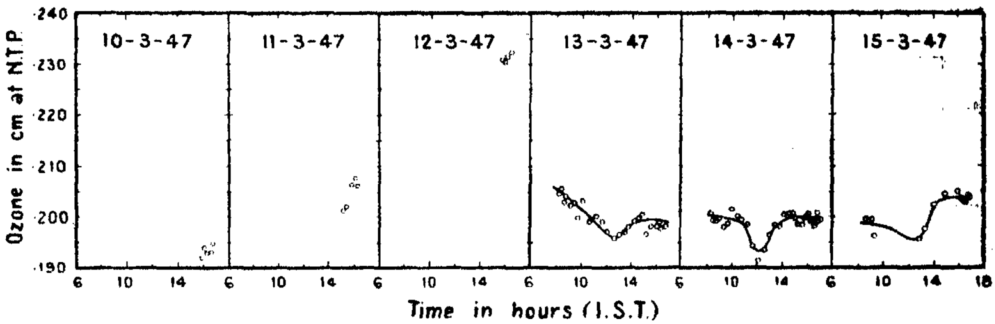

FIG. 7. Diurnal variation of ozone on consecutive days when the values of the ozone amount are falling

§6. DAY-TO-DAY VALUES OF ATMOSPHERIC OZONE

In India, whenever there is ground haze, even of small amount, it rises in the forenoon with the sun's heating of the ground and causes a disturbance in the course of the values of L. After the haze is dissipated by turbulence, the variation of L is smoother. For comparing day-to-day values of ozone, therefore, afternoon measurements were used. Only when afternoon observations could not be had for any reason, were morning observations used for the comparison.

Fig. 8 shows the daily mean afternoon values of the total amount of atmospheric ozone at Delhi during the period November 1945 to March 1947. These are on the basis of direct sun observations and generally refer to afternoon. The gaps correspond to days when cloudy weather prevented direct sun observations.

Table I gives the monthly mean values of ozone at Delhi during the period November 1945 to March 1947, and these are also shown graphically

TABLE I

Monthly mean values of atmospheric ozone at Delhi (28° 35′ N.)

n = No. of days of observations (direct sun only), *x* = Ozone in cm. at N.T.P.

Month	1945		1946		1947		Mean
	n	*x*	*n*	*x*	*n*	*x*	*x*
January ..			28	0·170	18	0·192	0·181
February ..			22	0·178	26	0·197	0·185
March ..			28	0·183	24	0·198	0·191
April ..			30	0·168			0·188
May ..			29	0·187			0·187
June ..			28	0·189			0·189
July ..			21	0·179			0·179
August ..			21	0·173			0·173
September ..			28	0·176			0·176
October ..			21	0·179			0·179
November ..	19	0·160	29	0·175			0·172
December ..	27	0·170	28	0·182			0·176

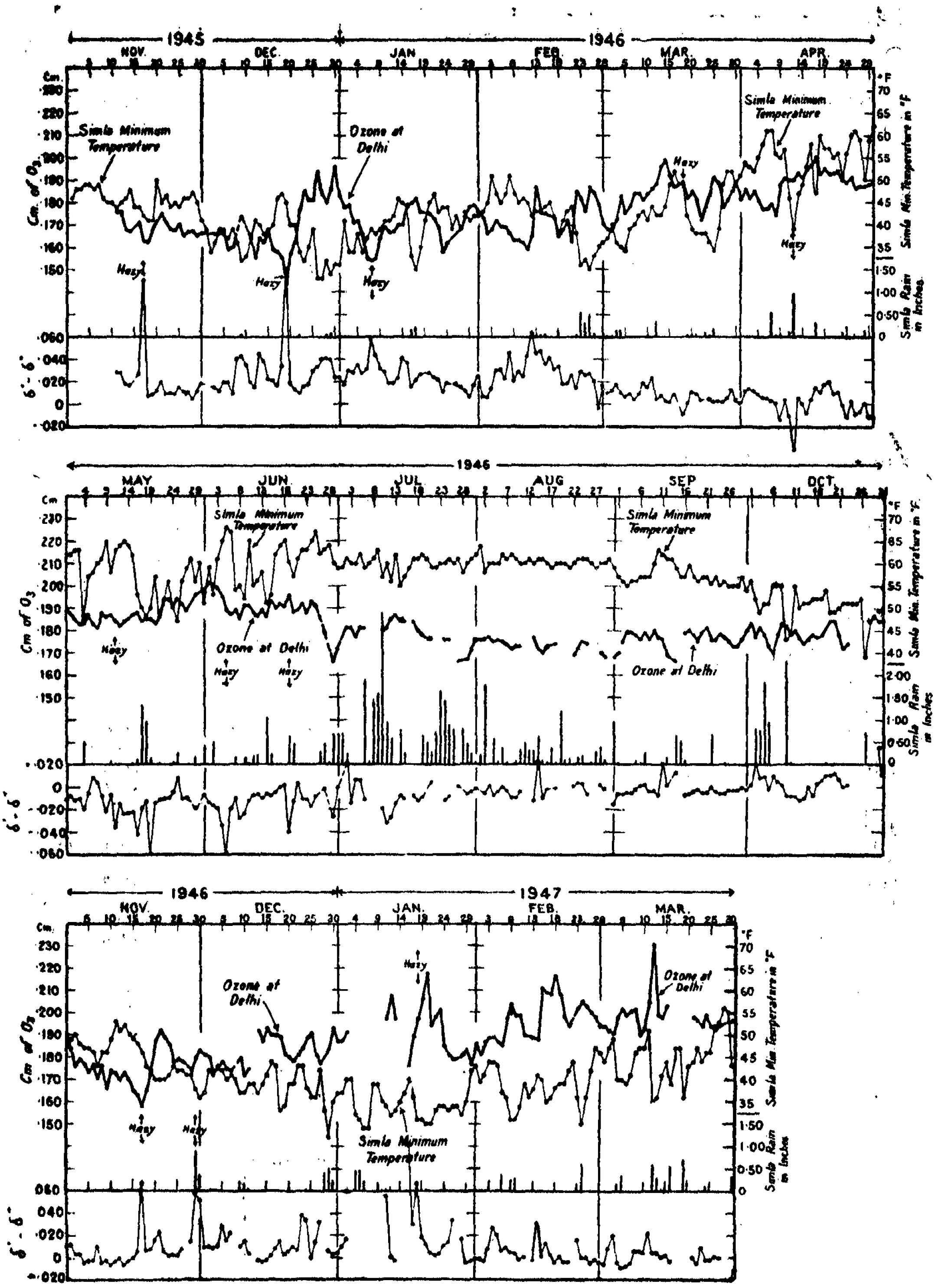

FIG. 8. Daily values of afternoon ozone amounts and atmospheric turbidity (δ′ − δ″) at Delhi and of minimum temperatures and rainfall recorded at 0800 hrs. at Simla, during November 1945 to March 1947.

in Fig. 9. Tables 2 to 5 and Fig. 10 give similar monthly data obtained previously with the old photographic instruments at Bombay,[11] Kodaikanal,[3] Helwan[3] and Zi-ka-wei[4] respectively.

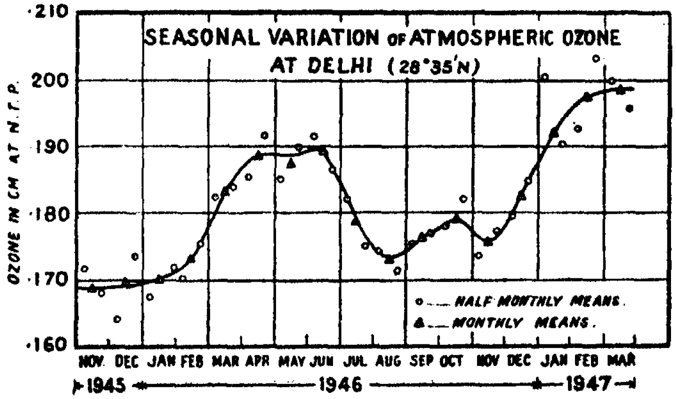

FIG. 9. Seasonal variation of atmospheric ozone at Delhi (28° 35′ N.)

TABLE II. *Monthly mean values of ozone at Bombay* (18° 54′ N.)
(From Dr. Chiplonkar's measurements)

Month	1936		1937		1938		Mean
	n	*x*	*n*	*x*	*n*	*x*	*x*
January			26	0·215	30	0·205	0·210
February			17	0·234	28	0·213	0·221
March			20	0·210	31	0·215	0·213
April			28	0·219	27	0·229	0·224
May			3	0·191	28	0·224	0·221
June			2	0·188	9	0·220	0·214
July			4	0·179	11	0·223	0·211
August			14	0·194	10	0·207	0·199
September			15	0·214	16	0·213	0·213
October	10	0·217	28	0·219			0·218
November	2	0·196	22	0·205			0·204
December	9	0·213	31	0·207			0·208

TABLE III. *Monthly mean values of ozone at Kodaikanal* (10° 10′ N.)
(From Dobson and Harrison's measurements of Kodaikanal plates)

Month	1928		1929	
	n	*x*	*n*	*x*
January			24	0·192
February			24	0·194
March			23	0·199
April			15	0·204
May			18	0·211
June			7	0·209
July			14	0·211
August			19	0·205
September	17	0·206		
October	12	0·2025		
November	7	0·193		
December	12	0·189		

TABLE IV. *Monthly mean values of ozone at Helwan (Egypt, 29° 50° N.)*

Month	1928 *n*	1928 *x*	1929 *n*	1929 *x*
January ..			23	0·233
February ..			18	0·237
March ..			15	0·250
April ..			17	0·246
May ..			..	..
June ..			..	..
July ..			8	(0·230)
August ..			20	0·231
September ..			23	0·232
October ..	9	(0·214)	6	(0·215)
November ..	16	0·207		
December ..	22	0·211		

TABLE V. *Monthly mean values of ozone at Zi-ka-wei (Shanghai, 31° N.)*

(From Rev. P. Lejay's measurements)

Month	1932	1933	1934	1935	1936	Mean
January ..	0·212	0·254	0·248	0·255	0·267	0·247
February ..	0·243	0·263	0·251	0·279	0·275	0·262
March ..	0·262	0·262	0·268	0·266	0·275	0·267
April ..	0·249	0·254	0·251	0·259	0·281	0·259
May ..	0·241	0·255	0·250	0·263	0·269	0·256
June ..	0·240	0·258	0·242	0·248	0·210	0·240
July ..	0·226	0·232	0·230	0·227	0·229	0·229
August ..	0·229	0·239	0·226	0·224	0·240	0·232
September ..	0·233	0·231	0·222	0·230	0·231	0·229
October ..	0·226	0·211	0·220	0·222	0·225	0·221
November ..	0·221	0·206	0·204	0·211	0·214	0·211
December ..	0·219	0·231	0·221	0·225	0·221	0·223

In general, the maximum ozone values occur in April-June. The minimum seems to occur in November but there is a pronounced secondary minimum in the monsoon months July-August. Curves for Kodaikanal and Bombay and also those for Helwan and Zi-ka-wei show similar features. Even for the same place, the monthly means for two successive years differ appreciably as is seen from both Bombay and Delhi data. At Delhi, for example, the ozone values for the winter of 1946–47 were definitely higher than those for the winter of 1945–46. Similar differences are observable in the Tromsø[16] data for the years 1939–42. Any definite latitude effect in the tropics cannot be established from the observations so far made in India.

On the average, the ozone amount over Delhi appears smaller than that over Bombay or Kodaikanal. It should be remembered that the photo-

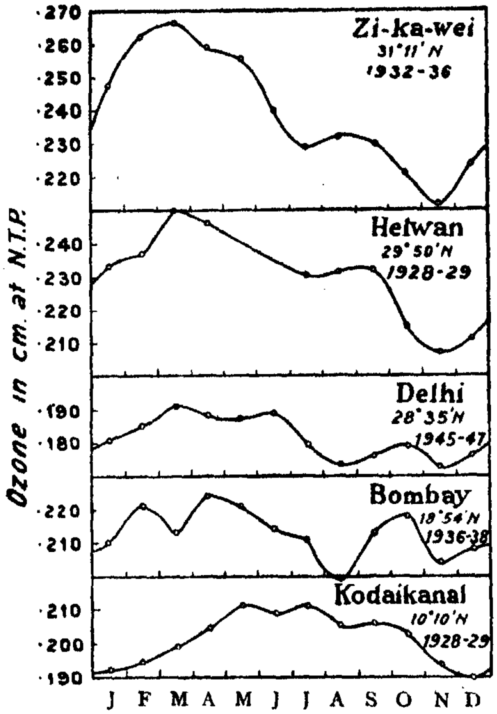

FIG. 10. Annual variation of atmospheric ozone in low latitudes

graphic instrument was used at the latter two places and that a modified formula with slightly different constants was used for calculating the ozone amounts over Delhi.

§7. DAILY VALUES OF (δ′–δ″), A MEASURE OF ATMOSPHERIC TURBIDITY

In obtaining the final equation 2 (1) for x, it was assumed that for the pair of longer wavelengths,

$$\log I''/I' = \log I_0''/I_0' + \alpha' x\mu + (\beta_1' - \beta_1'')\, m + (\delta' - \delta'')\, m \qquad (4)$$

where the symbols have the meaning stated in §2.

This leads to

$$(\delta' - \delta'')\, m = (L' - L'_0) - \alpha' x\mu - (\beta_1' - \beta_1'')\, m \qquad (5)$$

i.e.,
$$(\delta' - \delta'') = (L' - L_0')/m - \alpha' x .\ \mu/m - (\beta_1' - \beta_1'') \qquad (6)$$

If observations are taken for small values of m, the ratio μ/m is very nearly equal to unity and we get

$$\delta' - \delta'' \approx (L' - L_0')/m - \alpha' x - (\beta_1' - \beta_1'') \qquad (7)$$

Here the first term on the right-hand side of the equation corresponds to the incident radiation, the second term to the attenuation due to absorption by ozone, and the last to the attenuation due to molecular scattering. The left-hand side thus corresponds to the fraction of the incident radiation scattered by the large particles, and thus may be taken as a measure of the atmospheric turbidity in the long-wavelength region (3300 to 4450 A).

The above expression for $(\delta' - \delta'')$ can be easily calculated directly from the observations for the pair of longer wavelengths, if the value of x is roughly known and the value of $(\beta_1' - \beta_1'')$ for molecular scattering is assumed for the place of observation. Normally δ' is greater than δ'' and hence the expression $(\delta' - \delta'')$ should be positive. If, however, $(\delta' - \delta'')$ is found to be negative, it would mean either that (*a*) the attenuation due to particle scattering at 3300 A is *less than* that due to particle scattering at 4450 A, which is rather anomalous, or that (*b*) the instrument is analysing not directly transmitted sunlight alone, but an additional radiation richer in shorter wavelengths goes into the instrument. A value of $\delta' - \delta''$ nearly equal to zero would mean that the scattering corresponds to sufficiently large particles so as to make it practically neutral.

Daily values of $\delta' - \delta''$ were calculated along with the ozone values for the period November 1945 to March 1947 and these are tabulated in the Appendix, together with the remarks about the sky condition on each day. These are also plotted along with the ozone values in Fig. 8.

An inspection of the plot suggests the following general conclusions:—

(*a*) On average clear days, $\delta' - \delta''$ is positive during the period November to March, mostly negative during the period April to July, and near about zero during the rest of the year.

(*b*) On hazy days, the numerical value of $\delta' - \delta''$ increases with increase in haziness in all the seasons.

In a previous paper,[14] an explanation is given of the unexpected new feature about the negative sign of $\delta' - \delta''$ (*i.e.*, apparently greater loss due to scattering at 4450 A than at 3300 A) in the pre-monsoon period, particularly on days when there was widespread milky haze over the sky. A suitable modification in the formula for the calculation of the value of total ozone x was also suggested. Here, the values of $\delta' - \delta''$ are simply tabulated as a convenient measure of the atmospheric turbidity and may be compared with the remarks by visual observation about the sky condition.

§8. CORRELATION WITH METEOROLOGICAL FACTORS

The daily ozone values at Delhi were plotted side by side with various meteorological factors, such as the pressure at 0800 hrs. at Delhi and Simla, rainfall, minimum temperature, etc. Out of these, Simla minimum temperature showed a significant negative correlation with daily ozone values at Delhi during some non-monsoon months when western disturbances passed regularly. The minimum temperatures at Simla were, however, frequently affected by rainfall or fōhn action. This is clearly seen in Fig. 8, which gives daily ozone values at Delhi along with minimum temperatures and daily rainfalls at Simla. Although higher correlation was expected with upper air data, comparison with available upper winds and radiosonde temperatures at 6 km. over Delhi did not show any definite correlation.

Table VI gives the standard deviations and correlation coefficients between Delhi ozone amounts and Simla minimum temperatures both month

TABLE VI. *Correlation between Delhi ozone amounts (x) and Simla minimum temperatures (y)*

N= number of observations in the period

Month	N	Standard Deviation		Correlation Coefficient r	$Z = \frac{1}{2}\log_e\frac{1+r}{1-r}$	Standard error $\pm 1/\sqrt{N-3}$
		Ozone σx 10^{-3} cm.	Min. Temp. σy °F.			
November 1945 ..	19	3·9	2·3	+0·26	+0·27	±0·250
December 1945 ..	29	12·7	5·0	−0·86	−1·29	±0·196
January 1946 ..	29	7·7	4·3	−0·11	−0·11	±0·196
February 1946 ..	28	7·8	5·6	−0·63	−0·74	±0·200
March 1946 ..	29	7·4	5·7	+0·22	+0·23	±0·196
November 1945 to March 1946 ..	134	10·2	5·5	−0·20	−0·20	±0·087
April 1946 ..	30	6·2	5·3	−0·28	−0·29	±0·193
May 1946 ..	29	4·4	5·8	−0·36	−0·38	±0·196
June 1946 ..	28	7·2	4·9	+0·02	+0·02	±0·200
July 1946 ..	21	5·4	2·0	−0·31	−0·32	±0·236
August 1946 ..	21	2·8	0·9	−0·05	−0·05	±0·236
September 1946 ..	28	3·5	2·1	−0·17	−0·17	±0·200
October 1946 ..	25	4·6	3·2	−0·33	−0·34	±0·213
April 1946 to October 1946 ..	182	7·9	5·1	−0·13	−0·14	±0·075
November 1946 ..	29	7·9	4·4	−0·49	−0·54	±0·196
December 1946 ..	28	6·5	3·7	−0·19	−0·19	±0·200
January 1947 ..	20	10·9	3·8	−0·58	−0·66	±0·243
February 1947 ..	26	9·1	4·4	−0·40	−0·43	±0·209
March 1947 ..	24	7·9	4·5	−0·50	−0·55	±0·218
November 1946 to March 1947 ..	127	12·4	5·6	−0·37	−0·39	±0·090

by month and collectively for the three periods November 1945 to March 1946, April 1946 to October 1946 and November 1946 to March 1947. In December 1945 and February 1946, the correlations were high and negative (– 0·86 and – 0·63 respectively). In other months the correlations were less marked, and there are also three months with positive correlation. The last two columns give an idea of the significance of these correlations on applying the Z significance test.

The day-to-day changes in ozone amount were conspicuous during the period of western disturbances. In general, northerly air was found to be associated with high ozone amounts. Any association of changes of ozone amount with fronts has not yet been established. In the monsoon season, the average ozone amount was low and the day-to-day fluctuations were also small. The stabilizing effect of the monsoon on the total ozone amount in the atmosphere at a low value suggests that water vapour in the upper troposphere has a destructive action on ozone. During the monsoon, the tropopause in North India is almost always of Type I, beginning with a strong inversion at a height of 16–17 km. Mixing from below up to the tropopause would then be a normal feature.

§9. EFFECT OF THUNDERSTORMS

Direct sun observations before and after thunderstorms were made on a few occasions (11–4–46, 22–4–46, 30–4–46, 4–5–46, 20–5–46, 6–6–46, 15–8–46); observations were also made during thunderstorms with light rain falling from thundering cumulonimbus clouds overhead. In no case was any significant change in the ozone content observed. Later at Simla also, on 5–5–47, direct sun observations were made with thunder clouds all around and heavy hailstorms before and after observations; but no significant rise in ozone content was observed. The above result is at variance with Dobson's recent finding[10] that a sudden rise in ozone, within a short period of one or two hours, from 0·250 to 0·475 cm. occurred during a thunderstorm on 13th July 1941. He attributes this high rise in ozone to electrical disturbances during thunderstorms and states that 'most of the ozone formed during thunderstorms is almost certainly situated within the thunder cloud and not in the stratosphere. Such observations have necessarily to be made on the cloudy sky and are much less accurate than observations with sunlight. It is probable, however, that any error involved will make the observed value too small rather than too great'. Dobson's results were based on observations on cloudy zenith sky, but one would have expected similar changes to be observable with direct sun observations also in the neighbourhood of thundering clouds. The discrepancy remains to be explained.

There was only one occasion (13th March 1947) when an appreciable rise in ozone amount was noticed (from 0·190 to 0·230 cm.). But this thunderstorm occurred late in the evening, three to four hours after the high value of ozone was observed by means of direct sunlight observations. On that day, there was a depression over Rajputana, roughly 300 miles southwest of Delhi. Apparently, changes in ozone content associated with some western disturbances do occur, but changes directly connected with individual thunderclouds have been difficult to find.

§10. EFFECT OF MAGNETIC DISTURBANCES AND SUN-SPOTS

No quantitative correlation could be established between the daily magnetic character figures from records at Alibag and the daily ozone amounts. There were also no marked changes in ozone when big sunspots and associated solar disturbances were reported in the months of February and March 1946.

§11. CONCLUDING REMARKS

The marked correlation of ozone amounts with Simla minimum temperatures suggests that changes of air-mass at high levels containing appreciable quantities of ozone do occur in the season of western disturbances, northerly air from higher latitudes bringing with it more ozone. The day-to-day changes in ozone amounts are much less pronounced than in temperate latitudes. For an adequate study of the distribution of ozone in the field of cyclones and anti-cyclones, simultaneous observations at a few more stations are necessary. During the monsoon months, the ozone amount is insensitive to surface conditions, suggesting that tropical ozone exists mostly high up in the atmosphere in a region little disturbed by surface weather changes.

§12. ACKNOWLEDGMENTS

The observations were made with the Dobson spectrophotometer belonging to the India Meteorological Department and the author's thanks are due to the Director-General of Observatories for the use of the instrument and for giving all necessary facilities. The author wishes to express his grateful thanks to Prof. K. R. Ramanathan, who initiated the present scheme and under whose direction the work was carried out. Thanks are also due to the Board of Scientific and Industrial Research for the award of a Research Fellowship during the period in which the work was done.

SUMMARY

Daily measurements of the total amount of atmospheric ozone were made at Delhi with Dobson's photo-electric ozone spectrophotometer during

the period November 1945 to March 1947. The optical wedges in the instrument required a recalibration and this was done carefully by a detailed method using perforated metal gauzes of known extinction. The constancy of the calibration was checked on a number of occasions during the period of observations. The constants L_0 and L_0' of the instrument were determined from the plots of the observations on a number of selected clear days.

An attempt to study the diurnal variation of ozone on many clear days showed that the afternoon values were generally higher than the morning ones with a marked dip at about the local noon. But there were some days with practically constant ozone and very occasionally, days with afternoon values lower than the morning ones.

The daily afternoon values of ozone from direct sun observations were plotted throughout the period of observation along with a number of meteorological factors. Simla minimum temperatures showed a significant negative correlation with ozone amounts, particularly during the non-monsoon seasons when western disturbances were prevalent. The significance of this is discussed. The minimum temperatures on some days were considerably affected by rainfall or by föhn-effect. There is no evident relation between the daily ozone variations and the magnetic character figures or sun-spots. Duststorms, thunderstorms and cumulonimbus clouds did not show any significant changes in ozone. This result differs from Dobson's recent findings and requires further investigation.

As regards annual variations, the maximum ozone values occur in April-May and the minimum in November with another pronounced secondary minimum in August. This was in agreement with previous observations at Kodaikanal and Bombay and at Helwan and Zi-ka-wei. The ozone values in November 1946 to March 1947 were markedly larger than those in November 1945 to March 1946.

Daily values of $(\delta' - \delta'')$, where δ', δ'' are the net losses due to particle scattering at the wavelengths 3300 and 4450 A respectively, are tabulated. This can be taken as a convenient measure of the atmospheric turbidity in this wavelength region. An unexpected new feature is the negative sign of $\delta' - \delta''$ (that is, apparent greater loss due to scattering at 4450 A than at 3300 A) in the pre-monsoon period, particularly on days when there is a widespread milky haze over the sky.

On the whole, the results show that the day-to-day variations in ozone amounts are small during the monsoon, but quite conspicuous during the season of western disturbances. In general, northerly air is found to be associated with high ozone amounts.

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APPENDIX

Daily values of atmospheric ozone and of $(\delta' - \delta'')$, *a measure of atmospheric turbidity, at Delhi for four specimen months during the period November* 1945 *to March* 1947

SYMBOLS

x = ozone in cm. at N.T.P. according to the newly proposed equation (1),

$$= \frac{(L_0 - L) - K'(L' - L_0') - m\{(\beta_1 - \beta_1') - K'(\beta_1' - \beta_1'')\}}{\mu\{(\alpha - \alpha') - K'\alpha'\}}$$

where $K' = 0{\cdot}249$, $\alpha = 1{\cdot}275$, $\alpha' = 0{\cdot}074$,

$\beta_1 - \beta_1' = 0{\cdot}0965$, $\beta_1' - \beta_1'' = 0{\cdot}2515$,

$(\beta_1 - \beta_1')/(\alpha - \alpha') = 0{\cdot}080$;

$x_{D'}$ = ozone in cm. at N.T.P. according to Dobson's revised formula (2) and with the values of the constants used as given above,

$$= \frac{L_0 - L}{\mu(\alpha - \alpha')} - \frac{\beta_1 - \beta_1'}{\alpha - \alpha'} \cdot \frac{m}{\mu} = \frac{L_0 - L}{1{\cdot}201\,\mu} - 0{\cdot}080\, m/\mu\ ;$$

x_D = ozone in cm. at N.T.P. according to Dobson's formula (3) and with the same values of constants as used by Dobson.

$$= \frac{L_0 - L}{1{\cdot}17\mu} - \frac{0{\cdot}10}{1{\cdot}17} = \frac{L_0 - L}{1{\cdot}17\,\mu} - 0{\cdot}085\ ;$$

δ' = scattering coefficient for large particles at 3300 A for the whole of the atmosphere over Delhi.

δ'' = the same at 4450 A.

ABBREVIATIONS

b = clear blue sky, B = deep blue sky;

*z*₀ = slightly hazy, *z* = hazy, *Z* = very hazy;

*c*₀ = slightly cloudy, *c* = cloudy, *o* = overcast.

Date	December 1945					March 1946				
	Sky	$\delta'-\delta''$	x	$x_{D\phi}$	x_D	Sky	$\delta'-\delta''$	x	$x_{D\phi}$	x_D
1	o	..	..	..	..	b	0·010	0·168	0·170	0·173
2	o	..	..	..	..	c	0·013	0·167	0·170	0·173
3	b	0·015	0·166	0·169	0·173	c	0·017	0·171	0·174	0·177
4	b	0·012	0·166	0·169	0·172	c_0	0·011	0·183	0·185	0·188
5	c_0	0·019	0·168	0·172	0·175	c_0	0·007	0·175	0·177	0·180
6	b	0·019	0·159	0·163	0·167	c_0	0·009	0·178	0·180	0·183
7	c_0	0·009	0·160	0·162	0·165	c_0	0·004	0·184	0·185	0·188
8	z_0	0·040	0·163	0·171	0·174	c	0·009	0·184	0·186	0·189
9	z_0	0·043	0·174	0·183	0·186	c	0·019	0·181	0·185	0·188
10	b	0·035	0·175	0·183	0·185	b	0·015	0·184	0·187	0·190
11	b	0·019	0·164	0·169	0·171	b	0·024	0·186	0·191	0·195
12	b	0·015	0·155	0·159	0·162	b	0·004	0·188	0·189	0·193
13	B	0·045	0·164	0·173	0·176	B	0·007	0·195	0·197	0·200
14	b	0·038	0·162	0·170	0·173	c_0	0·003	0·199	0·199	0·203
15	b	0·022	0·167	0·171	0·174	b	0·002	0·192	0·193	0·196
16	B	0·021	0·159	0·164	0·166	c	0·009	0·187	0·189	0·192
17	c_0	0·017	0·158	0·161	0·164	o	..	..	..	..
18	c_0	0·033	0·155	0·162	0·164	z	−0·009	0·189	0·187	0·190
19	Z	0·120	0·143	0·169	0·171	b	0·001	0·182	0·183	0·186
20	b	0·019	0·157	0·161	0·164	b	0·011	0·185	0·187	0·191
21	b	0·013	0·161	0·164	0·167	b	0·009	0·181	0·183	0·186
22	b	0·010	0·177	0·179	0·182	z_0	0·004	0·172	0·173	0·176
23	b	0·017	0·185	0·188	0·191	o	..	..	..	..
24	b	0·018	0·181	0·185	0·188	b	0·005	0·183	0·185	0·188
25	b	0·029	0·182	0·188	0·191	B	0·002	0·191	0·191	0·194
26	z_0	0·033	0·194	0·201	0·205	b	0·003	0·189	0·190	0·193
27	z_0	0·041	0·184	0·193	0·197	b	0·003	0·178	0·179	0·182
28	b	0·041	0·180	0·189	0·192	b	0·006	0·181	0·182	0·185
29	b	0·040	0·186	0·195	0·199	b	0·013	0·185	0·188	0·191
30	b	0·025	0·196	0·201	0·204	B	0·004	0·189	0·190	0·193
31	c_0	0·024	0·181	0·187	0·190	c_0	0·001	0·181	0·182	0·185

Date	May 1946					September 1946				
	Sky	$\delta'-\delta''$	x	$x_{D\theta}$	x_D	Sky	$\delta'-\delta''$	x	$x_{D\theta}$	x_D
1	b	−0·008	0·187	0·185	0·188	z	−0·006	0·170	0·169	0·172
2	b	−0·011	0·185	0·183	0·186	b	−0·006	0·175	0·174	0·177
3	b	−0·011	0·183	0·181	0·184	b	−0·005	0·179	0·179	0·182
4	z	−0·020	0·184	0·180	0·183	b	−0·005	0·179	0·179	0·182
5	z	−0·006	0·187	0·185	0·189	z_0	−0·002	0·178	0·178	0·181
6	b	+0·008	0·183	0·185	0·188	b	+0·001	0·176	0·177	0·180
7	b	+0·004	0·181	0·182	0·185	b	+0·003	0·179	0·179	0·182
8	b	−0·008	0·188	0·186	0·189	z_0	−0·003	0·176	0·175	0·179
9	c_0	−0·021	0·186	0·182	0·185	b	−0·003	0·180	0·179	0·182
10	z	−0·007	0·187	0·186	0·189	b	−0·007	0·177	0·175	0·178
11	Z	−0·036	0·185	0·177	0·180	b	+0·020	0·176	0·181	0·184
12	z	−0·015	0·182	0·179	0·182	c_0	+0·002	0·169	0·169	0·173
13	z	−0·024	0·184	0·179	0·182	o	..	..	..	..
14	z	−0·023	0·185	0·181	0·183	c	+0·013	0·166	0·169	0·172
15	z	−0·022	0·187	0·183	0·186	o	..	..	..	..
16	z	−0·042	0·188	0·179	0·182	B	−0·007	0·179	0·178	0·181
17	z	−0·018	0·184	0·180	0·183	z	−0·006	0·180	0·179	0·182
18	z	−0·013	0·186	0·183	0·187	b	−0·004	0·178	0·178	0·181
19	Z	−0·060	0·186	0·174	0·176	b	−0·002	0·175	0·175	0·178
20	z	−0·014	0·183	0·180	0·183	B	−0·005	0·179	0·178	0·181
21	z	−0·011	0·186	0·184	0·187	B	−0·005	0·181	0·180	0·183
22	z	−0·010	0·194	0·192	0·196	b	0·000	0·176	0·176	0·178
23	z_0	−0·009	0·194	0·192	0·195	b	−0·003	0·176	0·175	0·178
24	B	−0·005	0·191	0·190	0·193	z_0	−0·006	0·178	0·177	0·180
25	b	+0·008	0·194	0·196	0·199	b	−0·006	0·177	0·176	0·179
26	z_0	−0·011	0·192	0·190	0·193	B	−0·003	0·175	0·175	0·177
27	z	−0·010	0·189	0·187	0·191	B	−0·003	0·173	0·173	0·175
28	o	..	..	..	..	B	−0·003	0·173	0·173	0·175
29	Z	−0·018	0·195	0·191	0·195	B	0·000	0·175	0·175	0·178
30	o	..	..	..	..	B	−0·002	0·179	0·179	0·182
31	b	−0·007	0·198	0·197	0·200					

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CLASSES OF THE n-DIMENSIONAL LORENTZ GROUP

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§1. Introduction

The Lorentz group in n-dimensions is the group of transformations which leaves invariant the quadratic form

$$(x, y) = x^1y^1 - x^2y^2 - x^3y^3 \ldots\ldots\ldots - x^ny^n \tag{1}$$

If the x's and y's are real variables, the group is defined in the field of real numbers. For the real orthogonal group the invariant form is $x^1y^1 + x^2y^2 + \ldots + x^n y^n$. We can pass from this to the first form by replacing x^1 by ix^1 and this suggests the device of deriving properties of the Lorentz group from those of the real orthogonal. But by introducing the imaginary variable we pass from the field of real numbers into the field of complex numbers. This calls for caution in passing from one group to the other. It is well known that there exist essential differences between the two groups. The Lorentz group, unlike the real orthogonal, is not compact. Again it has infinite irreducible representations not possessed by the latter (Dirac, 1945, Harish-Chandra, 1947). In this paper it is shown that the reduction to canonical forms and the consequent class-structure of Lorentz matrices is not that suggested by analogy with real orthogonal matrices.* The latter matrices can be reduced by matrices of the group to a direct sum of rotations, that is matrices of the type $c \equiv \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$ and at most one matrix of the type $f \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ or ± 1, depending on whether n is even or odd. Every matrix can be brought to the diagonal form in the field of all complex numbers. The device mentioned above suggests that the corresponding canonical forms for matrices of the Lorentz group are the direct sum of $\pm h \equiv \pm \begin{pmatrix} \cosh\phi & \sinh\phi \\ \sinh\phi & \cosh\phi \end{pmatrix}$ and an orthogonal canonical form, or ± 1 and an orthogonal form. These matrices like orthogonal matrices can also be brought to a diagonal form. However it is found that a different class of matrices exist with a canonical form beginning with a 3×3 matrix which cannot be brought to the diagonal form by any matrix even in the field of all complex numbers.

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* After completion of this work, my attention was drawn to a paper (Wigner, 1939), in which many of the results proved here are given for the special case $n = 4$.

§2. From (1) we see that the squared length of a vector in the space of the Lorentz group can be an arbitrary real number. As is well-known, a vector is called time-like, null or space-like according as its squared length is positive, zero or negative. The null vectors generate a surface called the light cone which divides the space into time-like and space-like regions. The time-like region is divided by the origin into two parts, the future and the past, according as the first component of a vector in it is positive or negative. The defining equation of a matrix l which keeps (1) invariant is

$$\tilde{l}gl = g \tag{2}$$

where $\tilde{l}$ is the transpose of l and g is the diagonal matrix with $+1$ in the first row and -1 in the remaining rows. Lorentz matrices can be divided into two sets, G_+ and G_- according as the first column vector, which by (2) is time-like is in the future or past direction. A matrix of G_+ transforms a future vector into a future vector and a past vector into a past vector. Hence the product of two elements of G_+ is in G_+. Also G_+ contains the unit matrix and so G_+ is a subgroup. In the same way the proper matrices (that is, those of positive determinant) of G_+ again form a subgroup.

In the sequel, we require the following lemma:†

[1] If u and v have components $(u^1, u^2, \ldots, u^n)$, $(v^1, v^2, \ldots, v^n)$ and u is a null or time-like vector and $(u, v) = 0$,

then v is space-like, for from

$$(u^1)^2 \geqslant (u^2)^2 + (u^3)^2 + \ldots + (u^n)^2$$
$$u^1v^1 = u^2v^2 + u^3v^3 + \ldots + u^nv^n$$

It follows that $(v^1)^2 < (v^2)^2 + (v^3)^2 + \ldots (v^n)^2$ except when u and v are dependent.

§3. If λ is an eigenvalue of l, λ^{-1} is also one, for λ^{-1} is an eigenvalue of l^{-1} and since, from (2) $l^{-1}\quad g^{-1}\tilde{l}g$, l^{-1} and l have the same eigenvalues. If λ be real, positive and $\neq 1$, put $\lambda = e^{\phi}$, $\phi \neq 0$. The eigenvectors v_1 and v_2 corresponding to e^{ϕ}, $e^{-\phi}$ can be taken as real. Then $(v_1, v_1) = (lv_1, lv_1) = e^{2\phi}(v_1, v_1)$. Thus $(v_1, v_1) = 0$, and similarly $(v_2, v_2) = 0$. Put $w_1 = c$

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† Bhabha, "The Theory of the Elementary Particles and their Interactions," Chapter 4.

$(v_1 + v_2)$ $w_2 = c(v_1 - v_2)$, where c is a real number. Then $(w_1, w_1) = -(w_2, w_2) = 2c^2(v_1, v_2) \neq 0$ by lemma [1] and $(w_1, w_2) = 0$. Also

$$\begin{aligned} lw_1 &= \cosh\phi\, w_1 + \sinh\phi\, w_2 \\ lw_2 &= \sinh\phi\, w_1 + \cosh\phi\, w_2 \end{aligned} \tag{3}$$

By a proper choice of c, $(w_1, w_1) = \pm 1 = \mp(w_2, w_2)$. Hence w_1, w_2 satisfy the conditions required by (2) for the first and second column vectors of a Lorentz matrix. If w be one such matrix then the matrix l^1 satisfying the equation $lw = wl^1$ will, because of (3), have $(\cosh\phi, \sinh\phi, 0, \ldots, 0)$ and $(\sinh\phi, \cosh\phi, \ldots, 0)$ as the components of its first two columns. l^1 then has the form $\begin{pmatrix} h & k \\ o & a \end{pmatrix}$. Because w is a Lorentz matrix $l^1 = w^{-1}\, l\, w$ is also one. Substituting l^1 for l in (2) we find that $k = 0$ and a is orthogonal. a can be reduced to a canonical orthogonal form a_0 by an orthogonal matrix b and hence l^1 can be reduced by the Lorentz matrix $1 \dotplus 1 \dotplus b$. Thus l is reduced to the direct sum $h \dotplus a_0$ by the Lorentz matrix $w(1 \dotplus 1 \dotplus b)$. The same method applies to the case when there is a real negative eigenvalue $\neq -1$. If this be $-e^{\phi}$ then the first matrix in the reduction will be $-h$.

§4. The matrices not included in the reduction given above are those whose eigenvalues are complex numbers and ± 1. The complex eigenvalues of l have unit modulus. For then we have $l(v_1 + iv_2) = (c + id)(v_1 + iv_2)$, where c, d are real numbers, $d \neq 0$, and v_1, v_2 are real and independent vectors. It follows that $lv_1 = cv_1 - dv_2$, $lv_2 = dv_1 + cv_2$. From these, and $(v, v) = (lv, lv)$ for any v, we get three equations for the scalar products (v_1, v_1) (v_2, v_2), (v_1, v_2)

$$\begin{aligned} &(1 - c^2)(v_1, v_1) + 2cd(v_1, v_2) - d^2(v_2, v_2) = 0 \\ &cd(v_1\ v_1) + (c^2 - d^2 - 1)(v_1, v_2) - ca(v_2, v_2) = 0 \\ &d^2(v_1, v_1) + 2cd(v_1, v_2) - (1 - c^2)(v_2, v_2) = 0 \end{aligned}$$

which have non-zero solutions only if the determinant of the matrix of the coefficients vanish, *i.e.*, when $p^3 + 4d^2p = 0$ where $p = c^2 + d^2 - 1$. Thus $p = 0$ *i.e.*, the eigenvalues have unit modulus. Putting $p = 0$, the relations between the scalar products become $(v_1, v_1) = (v_2, v_2)$, $(v_1, v_2) = 0$, and hence by lemma [1] they are both space-like. Since $v_1 + iv_2$ can be multiplied by an arbitrary factor, the squared length of each vector can be taken to be $+1$. Choosing θ_1, so that $c = \cos\theta_1$, $d = -\sin\theta_1$, we have

$$\begin{aligned} lv_1 &= \cos\theta_1 v_1 + \sin\theta_1 v_2 \\ lv_2 &= -\sin\theta v_1 + \cos\theta_1 v_2 \end{aligned}$$

As, in §3, l can be reduced by a Lorentz matrix whose last two columns are v_1, v_2 to $l_1 \dotplus c(\theta_1)$ and if l_1 has a complex eigenvalue $e^{i\theta_2}$, to $l_2 \dotplus c(\theta_2) \dotplus c(\theta_1)$, and so on till we obtain a Lorentz matrix t of dimensions $s \times s$, $(s \leqslant n)$, whose eigenvalues are all ± 1.

§5. To reduce this matrix* t we use the theorem that any real matrix with these eigenvalues can be reduced by a real matrix u to t_0, the direct sum of matrices, each of which has only $+1$ or only -1 on the principal diagonal and $+1$ immediately above this diagonal and the remaining elements zero. Suppose these component matrices arranged in a certain order are of dimensions $p_1 \times p_1$, $p_2 \times p_2, \dots$ and for this order the column vectors of u are $u_1, u_2, \dots u_s$. Then

$$\begin{array}{ll} tu_1 = \pm u_1 & tu_{p_1+1} = \pm u_{p_1+1} \\ tu_2 = \pm u_2 + u_1 & tu_{p_1+2} = \pm u_{p_1+2} + u_{p_1+1} \\ \dots\dots\dots\dots & \dots\dots\dots\dots\dots\dots\dots\dots \\ tu_{p_1} = \pm u_{p_1} + u_{p_1-1} & tu_{p_1+p_2} = \pm u_{p_1+p_2} + u_{p_1+p_2-1} \end{array} \tag{4}$$

and similar equations hold for the remaining matrices. From (4), for

$$r = 2, 3, \dots p_1, p_1+2, p_1+3, \dots p_1+p_2, p_1+p_2+2, \dots$$

$$(u_1, u_r) = (tu_1, tu_r) = (\pm u_1, \pm u_r + u_{r-1}) = (u_1, u_r) \pm (u_1, u_{r-1})$$

Therefore $$(u_1, u_{r-1}) = 0 \tag{5}$$

Similarly $$(u_{p_1+1}, u_{r-1}) = 0, \ (u_{p_1+p_2+1}, u_{r-1}) = 0 \tag{5$'$}$$

(i) If both p_1 and $p_2 > 1$, put $r = 2, p_1 + 2$ in (5) and $r = p_1 + 2$ in the first equation of (5)′, then

$$(u_1, u_1) = (u_1, u_{p_1+1}) = (u_{p_1+1}, u_{p_1+1}) = 0$$

which contradicts lemma [1]. This applies to any two component matrices. Hence only one matrix has dimension > 1. Without loss of generality we take this to be the first.

(ii) If $p_1 > 3$

$$(u_2, u_3) = (tu_2, tu_3) = (u_2, u_3) \pm (u_2, u_2)$$

Therefore $(u_2, u_2) = 0$

which together with (5) for $r = 2, 3$ again contradicts lemma [1]. So p_1 and hence $p_2, \dots \leqslant 3$.

(iii) If $p_1 = 2$ from (5), (5)′

$$(u_1, u_r) = 0 \text{ for } r = 1, 2, \dots s$$

and these equations contradict the linear independence of the vectors u_r.

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* Bhabha, *loc. cit.*, § 2.

Thus $p_1 = 1$ or 3 and $p_2, p_3, \dots = 1$. If $P = 1$, the reduced form is entirely diagonal and $tu_r = \pm u_r$ for all r. If u_l has the eigenvalue $+1$ and u_m has the eigenvalue -1,

$$(u_l, u_m) = (tu_l, tu_m) = -(u_l, u_m) = 0$$

which means that the subspace of the vectors with eigenvalue $+1$ is perpendicular to that of eigenvalue -1. We can find normalized orthogonal vectors in these subspaces and the full set will cover the whole s-dimensional Lorentz space of t since the vectors u_r are linearly independent. These orthogonal vectors form a Lorentz matrix which reduces t to the diagonal form with ± 1 on the diagonal.

If there is a 3×3 matrix let this be placed first, then $u_4, u_5, \dots u_s$ are eigenvectors of t and are space-like because they are all perpendicular to the nullvector u_1. Normalized orthogonal vectors formed from these vectors will form the last $s - 3$ vectors of a Lorentz matrix which will reduce to the direct sum of an irreducible 3×3 matrix and a diagonal one. This 3×3 matrix will have all its eigenvalues $+1$ or all -1.

§6. The reduced forms of Lorentz matrices are thus known except for the 3×3 irreducible matrices with eigenvalues all $+1$ or all -1. We first show that the former belong, considering only 3×3 matrices, to the proper subgroup of G_+. For obviously their determinant is $+1$ and they must satisfy the characteristic equation $(l - 1)^3 = 0$. Thus

$$(l^3)_{11} - 3\,(l^2)_{11} + 3\,(l)_{11} - 1 = 0 \tag{6}$$

where $(l^r)_{11}$ is the element in the first row and column of the rth power of l. If $(l)_{11} < 0$, then $(l^2)_{11} > 0$, $(l^3)_{11} < 0$, and the left side of (6) is < 0. Hence $(l)_{11} > 0$.

It is known (Murnaghan, 1938) that 4×4 Lorentz matrices of the proper subgroup of G_+ can be expressed as exp. gs, where s is a real anti-symmetric matrix. By fixing one of the space axes, this is seen to be true also for 3×3 Lorentz matrices. If now s be the matrix

$$\begin{pmatrix} 0 & a & b \\ -a & 0 & c \\ -b & -c & 0 \end{pmatrix}$$

then $r = gs$ has eigenvalues $\pm \phi, 0$ where $\phi^2 = a^2 + b^2 - c^2$ and therefore exp. gs has the eigenvalues $e^{\pm\phi}, 1$. When ϕ is not zero we obtain the reductions $h \dotplus 1$ and $1 \dotplus c$, which have an invariant axis in the space and time-like regions respectively. When $\phi = 0$, all the eigenvalues are $+1$ and there is only one invariant direction and that on the light cone. We now show that in this case the Lorentz matrices can be reduced to the exponential of the matrix r_0 where

$$r_0 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \quad \text{exp. } r_0 = \begin{pmatrix} \frac{3}{2} & 1 & \frac{1}{2} \\ 1 & 1 & 1 \\ -\frac{1}{2} & -1 & \frac{1}{2} \end{pmatrix} \tag{7}$$

If v, v_2, x are real vectors such that

$$rv = 0, \qquad rv_2 = v, \qquad vx = v_2 \tag{8}$$

then, if $a^2 + b^2 = c^2$, they have the components

$$\begin{pmatrix} -c \\ b \\ -a \end{pmatrix}, \begin{pmatrix} \frac{b}{a} + \frac{c}{a} t_1 \\ -\frac{c}{a} - \frac{b}{a} t_1 \\ t_1 \end{pmatrix}, \begin{pmatrix} -\frac{c}{a^2} - \frac{b}{a^2} t_1 + \frac{c}{a^2} t_2 \\ \frac{b}{a^2} + \frac{c}{a^2} t_1 - \frac{b}{a} t_2 \\ t_2 \end{pmatrix}$$

t_1, t_2 being arbitrary. We put $x = v_1$ when $t_1 = 1$, $t_2 = -\frac{a}{2}$ and $x = v_3$ when $t_1 = 1$, $t_2 = +\frac{a}{2}$ then

$$v_1 - v_3 = v \tag{9}$$

From (8), (9),

$$\begin{aligned} rv_1 &= v_2 \\ rv_2 &= v_1 - v_3 \\ rv_3 &= v_2 \end{aligned} \tag{10}$$

It can be seen by direct calculation that v_1, v_2, v_3 satisfy the conditions for the column vectors of a Lorentz matrix and if l is this matrix, from (10), $l^{-1} rl = r_0$ and hence l^{-1} (exp. r) $l =$ exp$\cdot$ r_0. So exp. r_0 is a canonical form for 3×3 irreducible Lorentz matrices, whose eigenvalues are all $+ 1$. Since, for all matrices r of the irreducible class, $r^3 = 0$, we get, if e be the unit matrix,

$$\text{exp. } r = e + r + \tfrac{1}{2}r^2 = \frac{e + \frac{1}{2}r}{e - \frac{1}{2}r}$$

and the Cayley parametric form for these matrices is therefore $\frac{1}{2}r$. Any Lorentz 3×3 matrix with eigenvalues all -1 on multiplying by $-e$ becomes a matrix with eigenvalues all $+ 1$ and hence can be reduced to the canonical form $-$ exp. r_0.

§7. The above analysis shows that every real $n \times n$ Lorentz matrix can be reduced within the group to the canonical form $l_0 \dotplus a_0$, where l_0 is one of the Lorentz matrices

$$\pm 1, \pm \begin{pmatrix} \cosh\phi & \sinh\phi \\ \sinh\phi & \cosh\phi \end{pmatrix}, \pm \text{exp.} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$$

and a_0 is a canonical real orthogonal form. For canonical matrices of the proper subgroup of G_+, we can take only the plus sign of l_0, and f and -1 cannot occur in the direct sum a_0. Hence these matrices can be expressed as exp. gs_0 where s_0 is the direct sum of one of the matrices

$$0, \begin{pmatrix} 0 & \phi \\ -\phi & 0 \end{pmatrix}, \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & +1 & 0 \end{pmatrix}$$

and matrices of the type $\begin{pmatrix} 0 & -\theta \\ \theta & 0 \end{pmatrix}$ all of which are antisymmetric. It can be shown easily that any l transforms a proper matrix of G_+ into a proper matrix of G_+ and gs_0 into gs where s is again antisymmetric. Hence all proper matrices of G_+ can be expressed as exp. gs and hence these matrices are connected to the unit matrix by the matrices exp. tgs as the real number t varies from 0 to 1.

I am greatly indebted to Dr. H. J. Bhabha for suggesting this problem, for his guidance and for allowing me to read the manuscript of his book on "The Theory of the Elementary Particles and their Interactions".

SUMMARY

We obtain the canonical forms which define the classes of the full Lorentz group in n-dimensions. Besides the forms expected by analogy with the orthogonal group, which can be reduced to the diagonal form in the field of complex numbers, there exists a canonical form whose first component matrix is the matrix $\pm$exp. r_0 given by (7) in Section 6. This 3×3 matrix characterizes a class of Lorentz matrices with equal eigenvalues, $+1$ or -1, which cannot be diagonalized even in the field of complex numbers.

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ETHYLATION OF QUERCETAGITRIN AND PREPARATION OF ISOPATULETIN PENTAETHYL ETHER

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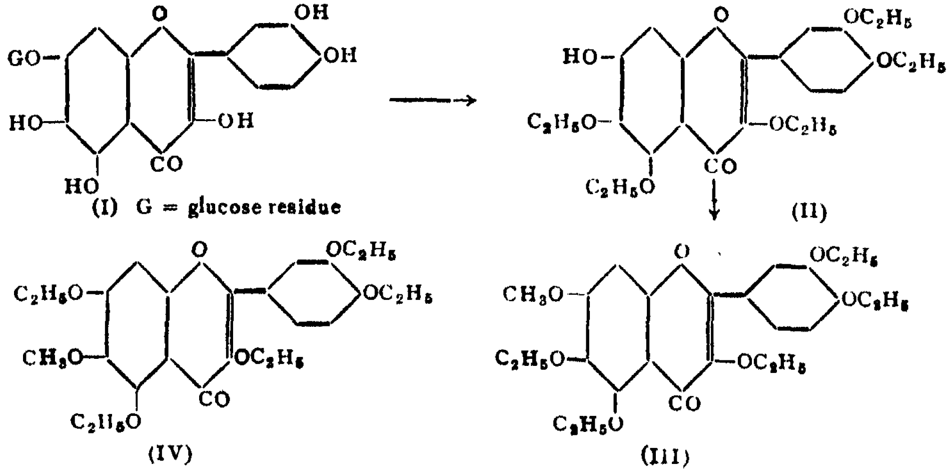
IN a previous paper[1] the constitution of quercetagitrin as the 7-glucoside of quercetagetin, was conclusively proved by providing synthetic evidence. For this purpose the glucoside was completely methylated and hydrolysed and the partial methyl ether thus produced finally ethylated. The reverse of this procedure, *i.e.*, ethylation of the glucoside, hydrolysis of the ethyl ether and final methylation will give a useful derivative not only for comparing it with a similar one obtained from patuletin by ethylation,[2] but also for establishing the constitution of the 7-methyl ether of quercetagetin, called here 'Isopatuletin', if it should occur in nature.

As it has already been mentioned in connection with gossypin[3] the ethylation of glycosides does not proceed satisfactorily with ethyl iodide. Diethyl sulphate is necessary for this purpose. Starting from quercetagitrin (I) the various stages involved in the present study are represented in the following formulæ. The mixed methyl ethyl ether (III) is different from *O*-pentaethyl patuletin (IV). Hence (III) is called iso-patuletin pentaethyl ether. This confirms that quercetagitrin is not a 6-glucoside.



(I) G = glucose residue

(II)

(IV)

(III)

EXPERIMENTAL

Ethylation of quercetagitrin (I)

Quercetagitrin (0·5 g.) was suspended in dry acetone (100 c.c.) and treated with freshly ignited potassium carbonate (6·0 g.) and diethyl sulphate (3 c.c.). After refluxing for 12 hours some more potassium carbonate (2·0 g.) and diethyl sulphate (2 c.c.) were added and the heating continued for a further period of 18 hours. The potassium salts were filtered and washed with warm acetone. From the filtrate the solvent was distilled off and water added. The semi-solid thus obtained was directly hydrolysed as given below.

7-*Hydroxy*-3 : 5 : 6 : 3′ : 4′-*pentaethoxy-flavone (II)*

The ethylated glucoside was treated with dilute sulphuric acid (40 c.c.; 7%) and refluxed over a wire-gauze for 2 hours. The solid that separated was filtered and washed with water. The monohydroxy compound crystallised from alcohol as colourless fine needles melting at 175–77°. It dissolved in aqueous sodium hydroxide to give an yellow solution, but did not give any colour with alcoholic ferric chloride. (Found: C, 65·3; H, 6·9; $C_{25}H_{30}O_8$, requires C, 65·5; H, 6·6%). Yield, 0·2 g.

7-*Methoxy*-3 : 5 : 6 : 3′ : 4′-*pentaethoxy flavone (III)*

The above 7-hydroxy compound (0·1 g.) was dissolved in dry acetone (15 c.c.) and treated with anhydrous potassium carbonate (2·0 g.) and dimethyl sulphate (0·4 c.c.). After refluxing for 8 hours, the potassium salts were filtered off and washed with warm acetone. On distilling off acetone from the filtrate and adding water to the residue, the monomethoxy-pentaethoxy flavone separated as a colourless crystalline solid. It crystallised from alcohol in the form of fine needles melting at 119–20°. Yield, 0·1 g. 6-Methoxy-3 : 5 : 7 : 3′ : 4′-pentaethoxy flavone[2] (ethyl patuletin) melts at 127–28°. The mixed melting point of the two substances was considerably depressed. (Found: C, 66·2; H, 7·1; $C_{26}H_{32}O_8$, requires C. 66·1; H, 6·8%.)

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A NOTE ON RESOKÆMPFEROL

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Resokæmpferol, 3 : 7 : 4′-trihydroxy flavone has not so far been found to occur in nature; however, the higher members, fisetin and robinetin and its ether, kanugin have been isolated from plants. The lower member 3 : 7-dihydroxy flavone is represented by its derivative, karanjin. Though the synthesis and study of resokæmferide, 3 : 7-dihydroxy-4′-methoxy flavone were reported by Heap and Robinson[1] and later by others,[2,3] the trihydroxy flavone, its trimethyl ether or acetate have not been described. Since they have been required in connection with other work done in this laboratory, they have now been made starting from ω-methoxy-resacetophenone and condensing it with anisic anhydride and sodium anisate according to the method of Allan and Robinson. The 7-hydroxy-compound first produced is methylated to yield the trimethyl ether and demethylated to form resokæmferol. Like the other members of this series this flavonol and its ethers exhibit strong fluorescence in solutions.

EXPERIMENTAL

7-*Hydroxy*-3 : 4′-*dimethoxy flavone*

ω-Methoxy-resacetophenone (2 g.) was condensed with anisic anhydride (9 g.) and sodium anisate (3 g.) by heating under reduced pressure at 170–80° for 3 hours. The reaction product was refluxed with 10% alcoholic potash (40 c.c.) for 20 minutes, the solvent distilled off, the residue dissolved in water and the deep brown solution saturated with carbon dioxide. The precipitated flavone was crystallised from alcohol when it separated out in the form of pale yellow prismatic needles melting at 248–50°. Yield, 1·5 g. (Found: C, 68·6; H, 5·0; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%.) It was sparingly soluble in alcohol and the solution did not exhibit any colour with ferric chloride. In concentrated sulphuric acid it showed weak blue fluorescence. The acetate of this crystallised from alcohol in the form of colourless needles melting at 148–49°.

3 : 7 : 4′-*Trihydroxy flavone*

The above 7-hydroxy compound (0·5 g.) was demethylated using acetic anhydride (3 c.c.) and hydriodic acid (5 c.c.). The trihydroxy flavone crystallised from alcohol in the form of glistening greyish yellow stout rectangular prisms melting with decomposition at 280°. (Found: C, 62·8; H, 4·5; $C_{15}H_{10}O_5$, H_2O requires C, 62·5; H, 4·2%.) Its alcoholic solution exhibited a green fluorescence and gave a deep violet brown colour with ferric chloride. Its solution in aqueous alkali had a green fluorescence while that in concentrated sulphuric acid had a bright peacock blue fluorescence. It did not give a precipitate with lead acetate.

The triacetate of the flavonol crystallised from alcohol in the form of colourless needles melting at 159–60°.

3 : 7 : 4'-*Trimethoxy flavone*

The 7-hydroxy compound (0·2 g.) was methylated in acetone medium (25 c.c.) with dimethyl sulphate (0·5 c.c.) and potassium carbonate (5 g.). The trimethyl ether crystallised from alcohol as colourless rectangular plates melting at 146–47°. (Found: C, 68·8; H, 5·5; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%.) Its solution in concentrated sulphuric acid was yellow with a greenish blue fluorescence.

SUMMARY

Resokæmpferol, its tri-acetate and tri-methyl ether are prepared and described.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XV. Further Synthesis of 7 : 8-Hydroxy-Flavonols Application of Dakins Reaction for Ortho-Oxidation

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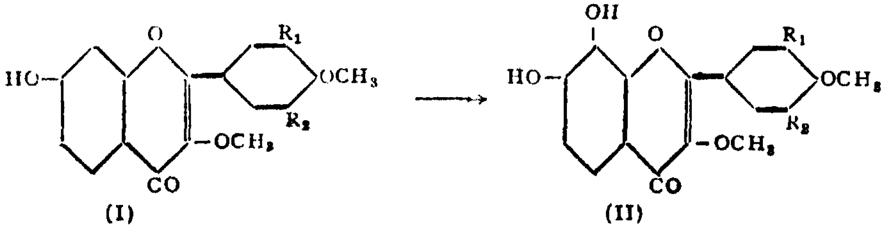
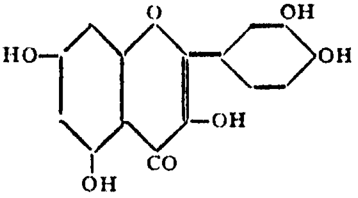
Nuclear oxidation by means of alkaline persulphate takes place readily in a position para to the activating hydroxyl group. On the other hand, ortho-oxidation of para-substituted phenols gives catechol derivatives in very poor yields or not at all. In an earlier publication[1] two favourable cases of ortho-oxidation in the flavone series were reported. 7-Hydroxy flavone and 3-methoxy-7-hydroxy flavone were employed for oxidation, the yields of the products being about 10 and 20% respectively. That they were 7: 8-dihydroxy flavone derivatives was definitely established. In continuation of this work higher members of the 7-hydroxy-flavonol series with one, two and three methoxyl groups in the side phenyl nucleus (I *a*, *b* and *c*) have now been oxidised with persulphate, the resulting products being considered by analogy to be members of the 7: 8-hydroxy-flavonol group (II*a*, *b* and *c*). The yields vary from 10 to 15%. Though these flavonols have not been so far discovered in nature, their occurrence seems to be quite possible and the present synthesis will render their future discovery easier. It should be remembered in this connection that anthoxanthins are far more varied in structure than the anthocyanins and several new types have been recently discovered.



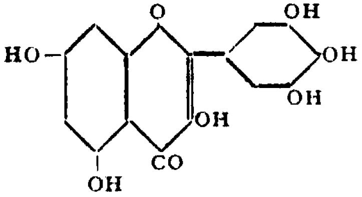
(I) (II)

(*a*) $R_1 = R_2 = H$
(*b*) $R_1 = OCH_3, R_2 = H$
(*c*) $R_1 = R_2 = OCH_3$

In the experiments on nuclear oxidation in the flavone series described so far, the problem of the condensed benzene nucleus has been carefully investigated. As far as the side phenyl nucleus is concerned the most important oxidation that could be expected from the theory of biogenesis[2] is represented by the conversion of quercetin (III) into myricetin (IV) in which a catechol unit undergoes change into a pyrogallol unit.

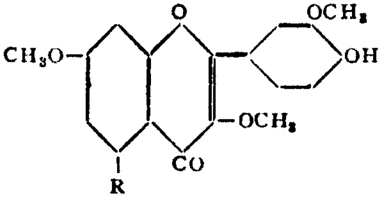


(III)

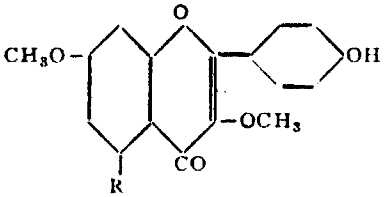


(IV)

Experiments have now therefore been carried out with alkaline persulphate to oxidise quercetin-tetramethyl-ether (V) and fisetin trimethyl ether (VI), but they are unsuccessful. Only minute quantities of impure products could be obtained which give brownish green ferric chloride colour. As simpler examples, kæmpferol trimethyl ether (VII) and 3: 7-dimethoxy-4′-hydroxy flavone (VIII) have also been employed with no better results.

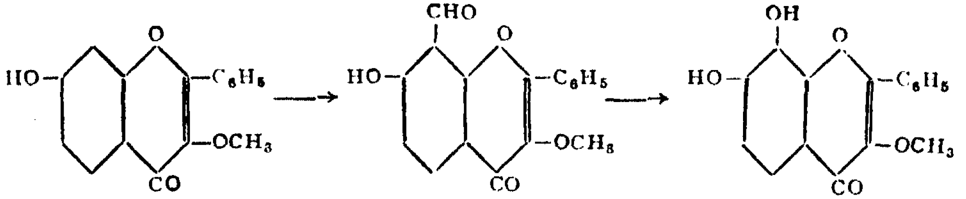


(V) R=OCH_3
(VI) R=H



(VII) R=OCH_3
(VIII) R=H

It has therefore to be concluded that this persulphate method is not suitable for ortho-oxidation in the side phenyl nucleus just as in many other cases also of benzenoid compounds in general. The more facile ortho-oxidation in the 8-position with this reagent seems to be in the nature of an exception depending upon the high reactivity of that position. There is no doubt, however, that ortho-oxidation does take place in the plant kingdom and particularly in the side phenyl nucleus of flavones. Only the laboratory analogy of nature's process does not seem to be the persulphate method in which a hydroxyl substitutes a nuclear hydrogen atom in a single stage. Some other process may be involved. It would appear that a multi-stage process as given below offers a better analogy: (1) converting the phenolic compound into an orthohydroxy aldehyde or ketone and (2) subjecting the aldehyde or ketone to oxidation with hydrogen peroxide (Dakin's reaction).[3] An ortho-dihydroxy compound results. Though Dakin's reaction has been successfully employed with simpler benzene derivatives particularly by Baker[4] in recent years, the only example[5] attempted in the flavone series (5-hydroxy-6-acetyl flavone) was reported unsuccessful. Consequently to begin with, it was considered necessary to test this reaction in the most favourable case among the flavones, 3-methoxy-7-hydroxyflavone. An aldehyde was preferred to a ketone as more likely to be produced in nature and the hexamine method of aldehyde preparation was chosen as more approximate to the biogenetic process. 3-Methoxy-7-hydroxy-flavone-8-aldehyde (X) has been prepared and described by Rangaswami and Seshadri[6] in the course of their synthetic work on flavonofurans. This compound is easily made in good yields by the action of hexamine on 3-methoxy-7-hydroxy flavone (IX). The chief difficulty in its oxidation with hydrogen peroxide is its low solubility in alkali. A sparingly soluble sodium salt is produced if the concentration of the alkali is even moderately high. But by suitably adjusting its strength and by adding pyridine a clear solution could be obtained and from this by the action of hydrogen peroxide almost quantitative yields of 3-methoxy-7:8-dihydroxy flavone (XI) could be secured. Thus the two stage process produces about 60% yield of the ortho-dihydroxy flavone as against the yield of 20% by the persulphate method. These highly successful exploratory experiments on ortho-oxidation offer promise of extension for the synthesis and for the study of the biogenesis of anthoxanthins and related compounds.



(IX) (X) (XI)

EXPERIMENTAL

7:8-Dihydroxy-3:4′-dimethoxy-flavone (II a)

To a stirred solution of 7-hydroxy-3:4′-dimethoxy-flavone[7] (I *a*) (2 g.) in aqueous sodium hydroxide (2 g. in 30 c.c.), potassium persulphate (4 g. in 60 c.c. of water) was added dropwise during the course of three hours. The solution was kept between 15° and 20° throughout the addition. After 24 hours, it was neutralised with hydrochloric acid, when the unchanged flavone separated out. It was filtered and the filtrate extracted twice with ether to remove the last traces of it. Concentrated hydrochloric acid (30 c.c.) was then added and the solution heated on the water-bath for half an hour. It became bright orange-red and a brown solid gradually separated. After cooling the solution, the solid was filtered and crystallised from alcohol when it was obtained in the form of straw coloured elongated rectangular prisms melting at 269–70°. Yield, 0·2 g. It gave a green colour with ferric chloride in alcoholic solution. (Found: C, 64·6; H, 4·3; $C_{17}H_{14}O_6$

requires C, 65·0; H, 4·5%.) Ether extraction of the filtered solution gave only a resinous product which could not be crystallised.

3 : 7 : 8 : 4′-*Tetramethoxy-flavone*

The above dihydroxy compound (0·2 g.) was refluxed in anhydrous acetone solution (30 c.c.) with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 g.) for six hours. The solvent was then distilled off and water added to the residue. The colourless solid product was filtered and crystallised from alcohol. It was obtained in the form of colourless soft needles melting at 143–4°. It gave no colour with alcoholic ferric chloride and was not soluble in aqueous alkali. Yield, 0·2 g. (Found: C, 62·9; H, 6·0; loss on drying 4·7; $C_{19}H_{18}O_6$, H_2O requires C, 63·3; H, 5·6; H_2O loss, 5·0%).

7 : 8-*Dihydroxy*-3 : 3′ : 4′-*trimethoxy-flavone* (*II b*)

7-Hydroxy-3 : 3′ : 4′-trimethoxy-flavone (I *b*)[8] (2 g.) was hydroxylated by means of potassium persulphate following the procedure already described. The dihydroxy flavone separated from the aqueous solution as a brown solid. On crystallisation from alcohol, it was obtained in the form of very pale yellow rectangular plates and needles melting at 236°. Yield, 0·2 g. It gave a deep green colour with alcoholic ferric chloride. (Found: C, 62·5; H, 4·6; $C_{18}H_{16}O_7$ requires C, 62·8 and H, 4·7%.)

3 : 7 : 8 : 3′ : 4′-*Pentamethoxy flavone*

The above compound (0·2 g.) was methylated with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 g.) in acetone solution (30 c.c.). It crystallised from alcohol in the form of colourless fibrous needles melting at 153–4°. Yield, 0·1 g. It gave no colour with alcoholic ferric chloride and was not soluble in aqueous alkali. (Found: C, 64·5; H, 5·4; $C_{20}H_{20}O_7$ requires C, 64·5 and H, 5·4%.)

7 : 8-*Dihydroxy*-3 : 3′ : 4′ : 5′-*tetramethoxy flavone* (*II c*)

Hydroxylation of 7-hydroxy-3 : 3′ : 4′ : 5′-tetramethoxy flavone[9] (I *c*) (2 g.) was effected with persulphate as in the other cases. The crude brown product was crystallised twice from alcohol when it was obtained in the form of aggregates of yellow rectangular plates melting at 229–30°. Yield, 0·3 g. It gave a grass green colour with alcoholic ferric chloride· (Found: C, 58·4; H, 4·8; $C_{19}H_{18}O_8$, H_2O requires C, 58·2 and H, 5·1%.)

3 : 7 : 8 : 3′ : 4′ : 5′-*Hexamethoxy flavone*

The dihydroxy flavone (II *c*) (0·2 g.) was methylated using dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 g.). The hexamethoxy flavone crystallised from alcohol in the form of colourless fibrous needles melting at 167°. Yield, 0·2 g. It gave no colour with ferric chloride and was not soluble in aqueous alkali. (Found: C, 62·7; H, 5·5; $C_{21}H_{22}O_8$ requires C, 62·7 and H, 5·5%.)

Oxidation of 3-methoxy-7-hydroxy-flavone-8-aldehyde (X)

The flavone aldehyde[6] (X) (0·4 g.) was treated with N/2 sodium hydroxide (4 c.c.), pyridine (5 c.c.) and water (1 c.c.). The clear solution was kept vigorously shaken and 6% hydrogen peroxide (2 c.c.) slowly run in the course of ten minutes. The yellow solution gradually turned reddish brown. It was allowed to stand for three hours with occasional shaking. By this time the colour of the solution had appreciably deepened. It was then acidified with concentrated hydrochloric acid whereby a yellow solid was precipitated. It was filtered, washed and dried. The crude product weighed 0·4 g. When extracted with cold alcohol in which the original aldehyde was sparingly soluble, it dissolved completely. On adding water little by little till turbidity developed and allowing to stand, pale yellow rectangular plates separated out melting at 221°. It agreed in all its properties with an authentic sample of 3-methoxy-7:8-dihydroxy-flavone and the mixed melting point was undepressed.

SUMMARY

In continuation of Part VIII, members of the 3-methoxy-7-hydroxy-flavone series with one, two and three methoxyl groups in the side phenyl nucleus are subjected to ortho-oxidation with alkaline persulphate; the yield of the corresponding 7:8-hydroxy compounds is 10 to 15%. On the other hand, attempts at ortho-oxidation by this method in the side phenyl nucleus have failed just as in several cases of simpler benzene derivatives. It is suggested that ortho-oxidation in nature should be considered to take place in multiple stages and this has been verified using a convenient example in the flavone series. 3-Methoxy-7-hydroxy-flavone undergoes change into the corresponding 8-aldehyde by the action of hexamine and this is converted into 3-methoxy-7:8-dihydroxy flavone by means of alkaline hydrogen peroxide, the yields being very good.

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FORMATION OF QUINONES BY OXIDATIVE DEALKYLATION

*Part II. Constitution of Pedicinin

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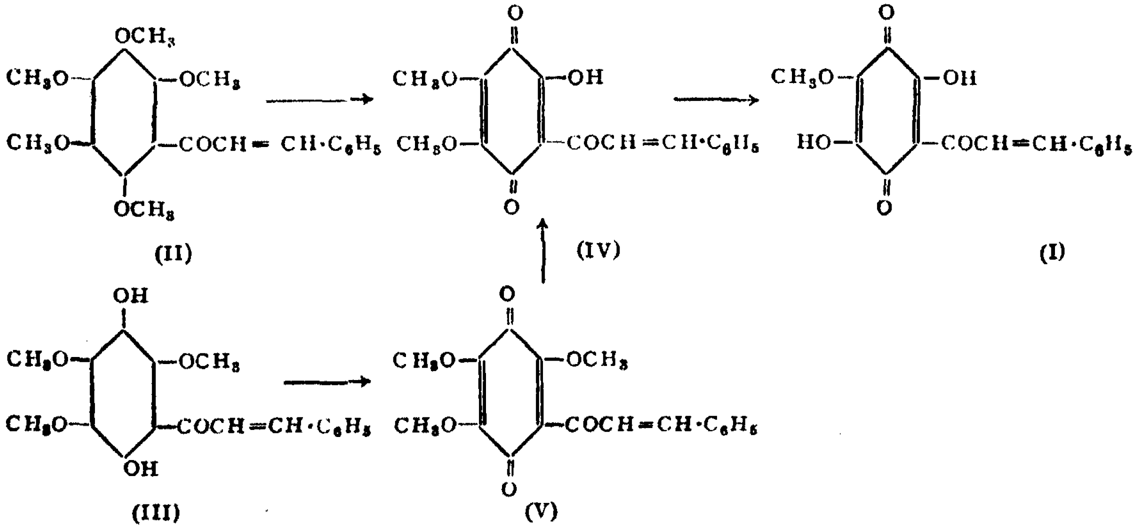
Besides its composition and properties the main information on the constitution of pedicinin (I) is derived from its preparation from pedicellin (II) and pedicin (III) involving oxidative demethylation. In the case of pedicellin, nitric acid has to be employed and methyl pedicinin (IV) can be obtained as an intermediate.[1] For the conversion of pedicin, bromine was first used and in this case the stages in the conversion could not be isolated and further dibromopedicin was a by-product.[1] [2] On the other hand, by employing benzoquinone or moist silver oxide as dehydrogenating agent it has been possible to isolate two intermediate stages, dimethyl (V) and monomethyl pedicinin[3] (IV).



The details of the constitution of pedicinin had formerly to be based to a considerable extent on theoretical considerations and on analogies.[3] For example, it was argued that a quinone carbonyl is capable of activating only one methoxyl group situated in the β-position of the katiœnoid system and further when there are two such methoxyls the one that suffers demethylation should be ortho to the ketonic carbonyl because it is activated by two katiœnoid systems. That the methoxyl in the 4-position is left out has also been shown by the analogy of 2-hydroxy-4-methoxy-3: 6-quino-acetophenone.[4] It is a very essential point but is not unequivocally established in a simple way by the above mentioned synthesis of pedicinin from pedicellin and pedicin. It has now been settled in an unambiguous manner by the process of ethylation which has been earlier adopted in the study of partial methyl ethers of flavones. For this purpose pedicinin is reduced using stannous chloride following the procedure of Salooja, Sharma and Siddiqui[3] to dihydropedicinin. From the properties of this compound it would appear that it does not have the chalkone structure (VI) but has undergone change into the corresponding flavanone (VII). But this point need not be specially considered here because, as a result of complete ethylation in the next stage, a chalkone is formed with four ethoxyl and one methoxyl groups. This product is found to be identical with 4-methoxy-2: 3: 5: 6-tetraethoxy chalkone (VIII) prepared synthetically starting from 2: 6-dimethoxy-quinol (IX). The various stages in this synthesis are as follows:—(1) Ethylation to form the quinol diethyl ether *i.e.*, 2: 6-dimethoxy-1: 4-diethoxy-benzene (X). (2) Friedel and Craft's reaction using acetyl chloride in ether solution. The product is 2-hydroxy-4-methoxy-3: 6-diethoxy-acetophenone (XI). This constitution is not only based on the analogy of this reaction with 1: 2: 3: 5-tetramethoxy benzene[5] but is also confirmed by the capacity of the compound to undergo presulphate oxidation, thus indicating the presence of a free nuclear position para to the phenolic hydroxyl group. (3) Nuclear oxidation of the above ketone with alkaline persulphate to (XII) and (4) complete ethylation using diethyl sulphate yielding 4-methoxy-2: 3: 5: 6-tetraethoxy acetophenone (XIII). (5) Condensation of the ketone with benzaldehyde to form the corresponding chalkone, 2: 3: 5: 6-tetraethoxy-4-methoxy chalkone (VIII).

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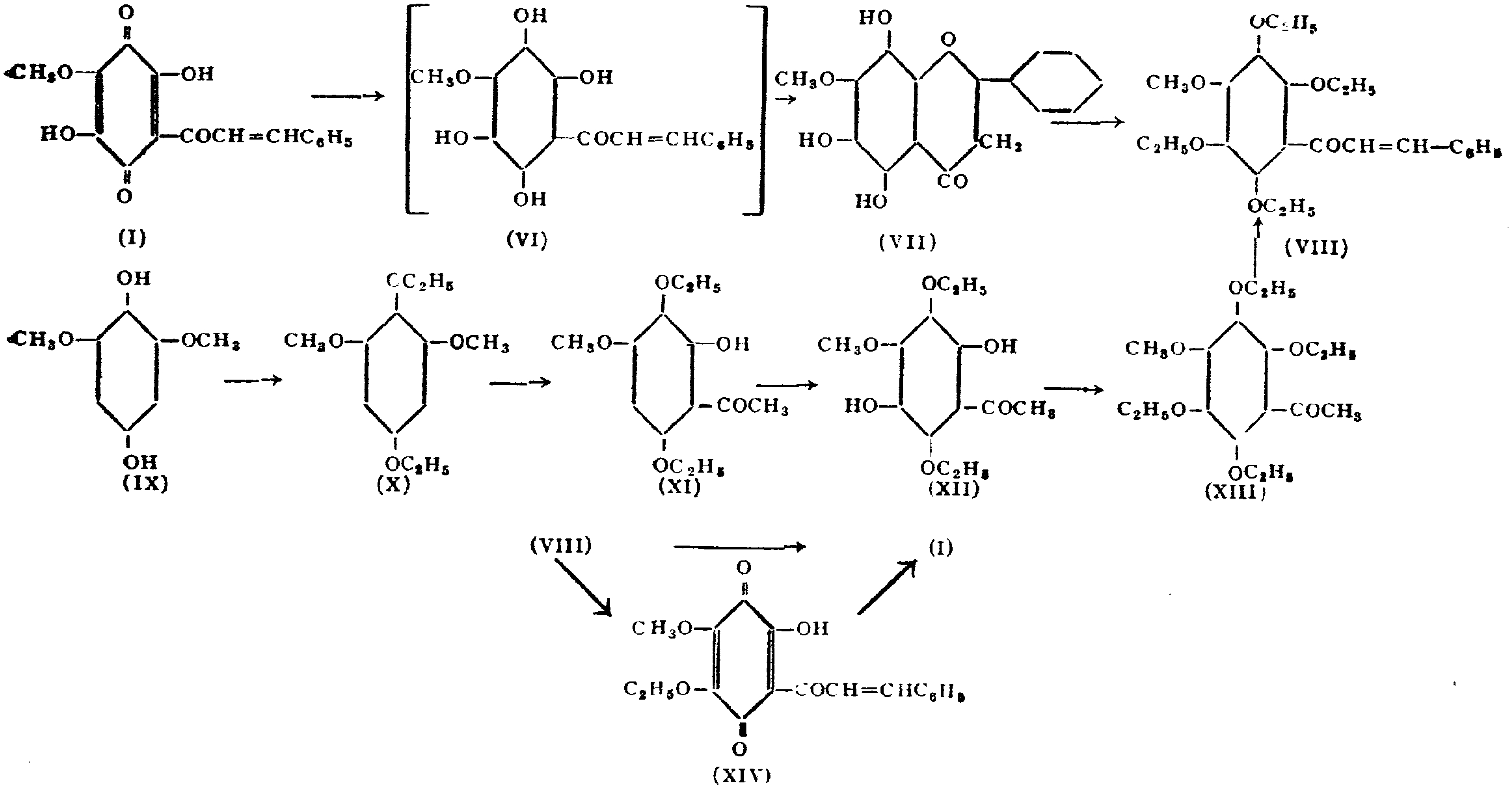
* The paper published in this journal 1948, 27, 245 may be considered as Part I.

The abovementioned tetraethoxy-monomethoxy-chalkone (VIII) as well as tetraethyl-dihydropedicinin undergo oxidation with nitric acid forming ethyl pedicinin (XIV) and pedicinin (I) as products. Thus all the ethyl groups can be removed in this reaction and it is strictly analogous to pedicellnin-pedicinin conversion.[3] This confirms that the progress of the reduction and ethylation of pedicinin has been as expected because the reverse process is effected by nitric acid and the original compound (pedicinin) is again obtained.


(I)
(VI)
(VII)
(VIII)
(IX)
(X)
(XI)
(XII)
(XIII)
(VIII)
(I)
(XIV)

In the course of this work, we have examined the toxic properties of 2:4:5-trimethoxy-3:6-quino-chalkone which is the immediate oxidation product of pedicin. In a concentration of 100 mg. per litre it exhibits strong toxic effect on fish (*Haplochylus panchax*) which lose balance and turn upside down in 11 minutes. The fish do not recover on removal to fresh water after this period and they die rapidly. But at a concentration of 50 mg. per litre no appreciable toxic effect could be noticed. Though this compound would appear to be weaker than pedicin in regard to the rapidity with which toxic effect is exhibited (*cf.* turning time for pedicin 3½ minutes for 100 mg. per litre), this quinone appears to be eventually stronger in its toxic effect because the fish die at this concentration whereas in the case of pedicin such death did not occur after removal to fresh water.

EXPERIMENTAL

Dihydropedicinin (VII)

The reduction of pedicinin was carried out according to the procedure of Salooja, Sharma and Siddiqui,[2] the amount of stannous chloride used being lowered to 15 g. per gram of pedicinin. The product was purified by crystallisation from hot aqueous alcohol and later from a mixture of ethyl acetate and benzene when it formed pale yellow silky needles melting at 162–63°. It was easily soluble in alcohol but sparingly in ether. In 5% aqueous sodium carbonate, it gradually dissolved to a yellow solution. In 5% sodium hydroxide it readily formed a deep red solution which changed to yellow on shaking with air. With ferric chloride in alcoholic solution a deep brown colour was obtained and with lead acetate an immediate pinkish brown precipitate. When the alcoholic solution was treated with *p*-benzoquinone, a deep red colour resulted immediately. Contrary to the reports of Salooja, *et al.*, the alcoholic solution of the substance was stable and no change could be observed on boiling.

Ethylation: Tetraethyl-dihydropedicinin (VIII)

A solution of dihydropedicinin (2 g.) in anhydrous acetone (25 c.c.) was treated with diethyl sulphate (5 c.c.) and anhydrous potassium carbonate (15 g.). The mixture was refluxed for 15 hours with occasional shaking. The solvent was then distilled off and the residue treated with water (200 c.c.). The mixture was extracted with ether twice and the ether extract shaken with 5% aqueous sodium hydroxide. After washing with water, it was dried over anhydrous sodium sulphate and the ether distilled when a brownish yellow liquid product was obtained. It did not crystallise on keeping in the ice-chest for a long time. In an attempt to purify it, the liquid was dissolved in a small quantity of ether and the solution treated with excess of light petroleum. The mixture was heated to boiling and the clear very pale yellow solution decanted from the brown insoluble matter. On concentrating it only a pale yellow viscous oil was obtained and it did not crystallise though it had been rendered pure. It was not soluble in aqueous alkali and did not give any colour with ferric chloride in alcoholic solution. It was characterised as the phenyl hydrazone as described below:—

The above product (0·5 g.) was treated with phenylhydrazine (0·5 c.c.) and glacial acetic acid (2 drops). The viscous mixture was heated in a boiling water-bath for one hour, cooled and poured into ice-cold dilute hydrochloric acid (100 c.c.). The mixture was extracted with ether twice and the ether extract shaken successively with dilute hydrochloric acid, aqueous sodium hydroxide (5%) and water. It was then dried over calcium chloride and distilled. The residual thick viscous mass, on dissolving in a small quantity of ether and cooling, deposited an almost colourless crystalline solid which was filtered and washed with a little ether. Crystallisation from alcohol gave glistening colourless big rectangular plates and prisms melting at 147–49°. (Found: C, 71·4; H, 7·5; $C_{30}H_{38}O_5N_2$ requires C, 71·4; H, 7·1%.) Yield, 0·3 g.

Oxidative dealkylation of tetraethyl-dihydropedicinin; Ethyl pedicinin (XIV) and pedicinin (I)

A solution of tetraethyldihydropedicinin (1 g.) in glacial acetic acid (3 c.c.) was treated with concentrated nitric acid (1 c.c.). The solution which immediately turned deep red was stirred well for 2 minutes and diluted with water (100 c.c.). An orange red sticky mass separated out which solidified when kept in the ice-chest for 3 hours. It was filtered, washed well with water and dried. When crystallised from a mixture of benzene and ligroin two fractions were obtained. The first one consisted of carmine red rectangular prisms melting at 202–3° alone or in admixture with an authentic sample of pedicinin; yield, 0·3 g. The second fraction, an orange yellow solid, was recrystallised from a mixture of benzene and ligroin. It formed orange coloured rectangular prisms melting at 113–14°. (Found: C, 65·4; H, 5·2; $C_{18}H_{16}O_6$ requires C, 65·8; H, 4·9%.) Yield, 0·4 g. This compound designated ethyl pedicinin as analogous to methyl pedicinin, was readily soluble in alcohol and benzene, sparingly in ether and very slightly in ligroin. It was easily soluble in aqueous sodium bicarbonate giving a reddish brown solution. It gave a deep red colour with ferric chloride in alcoholic solution.

Conversion of ethyl pedicinin into pedicinin

Ethyl pedicinin (0·2 g.) was dissolved in 5% aqueous sodium hydroxide (25 c.c.) and the clear red solution was acidified with concentrated hydrochloric acid after two minutes. The orange red solid was filtered, washed and crystallised from benzene. *It formed carmine red rectangular plates and prisms melting at 202–3° and identical with pedicinin.*

2-*Hydroxy*-4-*methoxy*-3 : 6-*diethoxy-acetophenone* (*XI*)

2 : 6-Dimethoxy-1 : 4-diethoxy benzene (X) was made by the ethylation of 2 : 6-dimethoxy quinol[6] with diethyl sulphate and potassium carbonate in dry acetone medium. It will be described in detail in another connection.

Powdered anhydrous aluminium chloride (23 g.) was dissolved in dry ether (60 c.c.) with cooling and then a solution of 2 : 6-dimethoxy-1 : 4-diethoxy benzene (25 g.) in dry ether (60 c.c.) added. To the mixture which was vigorously shaken and cooled in an ice-bath was added acetyl chloride (12 c.c.) in small quantities during the course of an hour and the shaking continued occasionally for another four hours keeping the mixture in the ice-bath. A heavy dark greenish brown oily layer first separated out and slowly changed into a yellowish green hard mass. After the mixture was allowed to stand for 24 hours, the supernatant ether layer was decanted off and crushed ice and concentrated hydrochloric acid (30 c.c.) were added to the remaining solid and vigorously stirred. The reaction mixture was then heated on a water-bath for 30 minutes to complete the decomposition of the aluminium chloride complex. While still hot, it was extracted with benzene twice and the benzene layer washed with dilute hydrochloric acid. It was then shaken repeatedly with 5% aqueous sodium hydroxide and the combined alkaline extracts acidified with concentrated hydrochloric acid. The pale yellow crystalline solid that separated out was filtered and washed with water. Yield, 25 g. Crystallisation from alcohol yielded very pale yellow prismatic needles melting at 104–5°. (Found: C, 61·5; H, 7·5; $C_{13}H_{18}O_5$ requires C, 61·4; H, 7·1%). In alcoholic solution it gave a reddish violet colour with ferric chloride.

2-*Hydroxy*-4-*methoxy*-3 : 6-*diethoxy chalkone*

To a solution of the above ketone (10 g.) in alcohol (100 c.c.) was added benzaldehyde (40 c.c.) and the mixture treated with strong aqueous potash (80 g. in 80 c.c.) with cooling. Sufficient alcohol was then added to get a clear homogeneous solution. The flask was tightly stoppered and left at the laboratory temperature for three days. The dark red reaction mixture was then poured into water (1,000 c.c.) and filtered from an amorphous yellow solid that separated out. The clear alkaline filtrate was extracted with ether and acidified with concentrated hydrochloric acid. The chalkone separated out as an orange coloured solid which was filtered and washed with aqueous sodium bicarbonate followed by water. Crystallisation from alcohol gave it in the form of long orange needles melting at 135–36°. (Found: C, 68·7; H, 6·6; $C_{20}H_{22}O_5$, $\frac{1}{2}H_2O$ requires C, 68·4; H, 6·5%.) It was sparingly soluble in aqueous sodium hydroxide and in alcoholic solution gave a deep reddish brown colour with ferric chloride. Yield, 9 g. Oxidation of this chalkone with alkaline persulphate did not proceed satisfactorily.

2: 5-*Dihydroxy*-3: 6-*diethoxy*-4-*methoxy acetophenone* (*XII*)

2-Hydroxy-4-methoxy-3: 6-diethoxy acetophenone (10 g.) was dissolved in aqueous potassium hydroxide (9 g. in 50 c.c.) and the clear solution, while being stirred and cooled at 15–20°, was treated dropwise with a solution of potassium persulphate (15 g. in 250 c.c.) and aqueous potash (9 g. in 30 c.c.) during the course of 2 hours. The deep brown reaction mixture was allowed to stand for 24 hours and neutralised to Congo Red using hydrochloric acid. The unchanged ketone separated as a brown solid which was extracted twice with ether. The clear brown aqueous solution was then treated with sodium sulphite (2 g.), concentrated hydrochloric acid (50 c.c.) and benzene (100 c.c.) and the mixture refluxed for 30 minutes. The benzene layer was separated and the extraction repeated with some more benzene (50 c.c.) for 15 minutes. The combined benzene extracts were separated, washed with a small quantity of water and dried over anhydrous sodium sulphate. After distilling off the solvent, the dihydroxy ketone was left behind as a brownish yellow crystalline solid. It was recrystallised from a mixture of alcohol and aqueous sulphur dioxide when it separated out as glistening pale yellow leaflets melting at 131–32°. (Found: C, 58·0; H, 7·0; $C_{13}H_{18}O_6$ requires C, 57·8; H, 6·7%.) It was easily soluble in alcohol and benzene but sparingly in water. In aqueous sodium hydroxide it formed a yellowish brown solution. With ferric chloride in alcoholic solution it gave an evanescent green colour which changed to deep brown red. Yield, 3·5 g.

2: 3: 5: 6-*Tetraethoxy*-4-*methoxy chalkone* (*VIII*)

The dihydroxy ketone described above (3 g.) was ethylated in anhydrous acetone medium (50 c.c.) with diethyl sulphate (8 c.c.) and anhydrous potassium carbonate (20 g.). On working up as usual, the ethyl ether (XIII) separated out as a brownish yellow viscous liquid (yield, 2·8 g.). This did not crystallise even on keeping in the ice-chest for a number of days. It was insoluble in alkali and did not give any colour with ferric chloride and was therefore directly used for the subsequent chalkone condensation. For this, a solution of the ethylated ketone (2 g.) in alcohol (15 c.c.) was treated with benzaldehyde (6 c.c.) and strong aqueous potash (15 g. in 10 c.c.). Sufficient alcohol was then added to get a clear solution which was allowed to stand for 2 days. The mixture was poured into water (300 c.c.) and extracted with ether. The ether extract was distilled off employing a current of steam in the final stages to remove benzaldehyde and benzyl alcohol. The chalkone left behind was taken up in ether, the solution dried over calcium chloride and purified by treatment with light petroleum as described under tetraethyl-dihydropedicinin. The pale yellow viscous oil that was obtained did not crystallise and was therefore characterised in the form of the phenyl hydrazone which was made according to the procedure already described for the natural sample. It crystallised from alcohol as colourless rectangular prisms melting at 147–49°. The melting point was undepressed when mixed with the sample prepared from dihydro-pedicinin.

This synthetic sample of tetraethoxy-methoxy-chalkone underwent oxidative de-ethylation with nitric acid to yield ethyl pedicinin and pedicinin.

SUMMARY

An essential point which has not been established in a simple manner by the previous study of pedicinin and its synthesis relates to the position of the methoxyl group. This has now been settled in an unambiguous manner by the reduction of pedicinin with stannous chloride to dihydropedicinin and its ethylation. The product is found to be identical with 4-methoxy-2:3:5:6-tetraethoxy chalkone obtained synthetically starting from 2:6 dimethoxy quinol. This chalkone undergoes oxidative de-ethylation with nitric acid yielding ethyl pedicinin and eventually pedicinin.

The toxic properties of dimethyl pedicinin (2:4:5-trimethoxy-quino chalkone) have been studied using fish.

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3.	Rao and Seshadri	.. *Proc. Ind. Acad. Sci.*, A, 1948, **27**, 375.
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SULPHUR DYES AND SULPHURISED VAT DYES

Part I. Constitution of Hydron Blue

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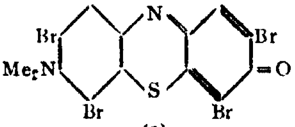
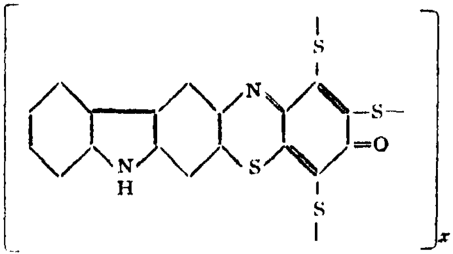
Attempts to determine the constitution of the sulphur dyes have so far had only limited success on account of the intrinsic difficulties of the problem: the amorphous and uncrystallisable character of the dyes; their instability and insolubility as a result of which molecular weight determinations have not been made; their variability of composition, and their tendency on treatment with reagents to undergo total decomposition or a breakdown to products which are as difficult to isolate in pure form as the parent dyes themselves.[1] The chemistry of Hydron Blue, which can be regarded as representative of a group of sulphur and sulphurised vat dyes obtained by thionation of indophenols, has now been re-examined. The important dye, Hydron Blue, is prepared by the thionation of carbazole-indophenol which is obtained by the condensation of carbazole and *p*-nitrosophenol. The imports[2] of the dye into India during 1937–38 were 1,45,433 lbs. of the value of Rs. 3,24,163. An interesting and commercially significant feature of Hydron Blue is the use of carbazole as a starting material, a product which is readily available as a bye-product in the isolation of pure anthracene from crude anthracene. Hydron Blue R and RR are useful for the production of navy and dark blue shades on cotton, especially in piece dyeing, and were marketed as competitors to indigo. The dyeings are carried out from the yellow alkaline hydrosulphite vat. In fastness properties Hydron Blue is superior to the Sulphur Blues, but inferior to anthraquinone vat dyes, the fastness figures for light, washing and chlorine being 6, 4–5 and 3 respectively.

The character of the sulphurised indophenols as thiazine derivatives was indicated by Meyenberg and Levy[3] and by Gnehm and Kaufler.[4] The latter workers found that Immedial Pure Blue, a dye prepared by the thionation of 4-dimethylamino-4′-hydroxydiphenylamine, when heated with potassium bromate and hydrogen bromide gave Tetrabromo-Methylene Violet (I) which was identical with the product obtained from Methylene



(I)

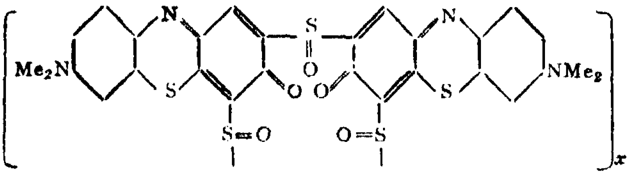
Blue by similar treatment. Many years later Weinberg[5] suggested the constitution (II) for Hydron Blue without giving any analytical or other



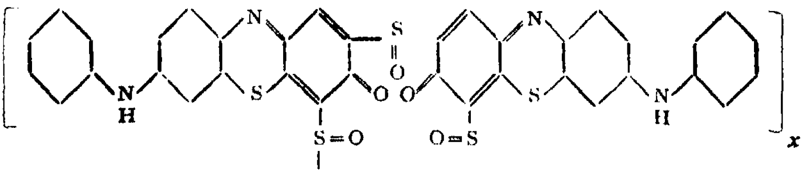
(II)

evidence.

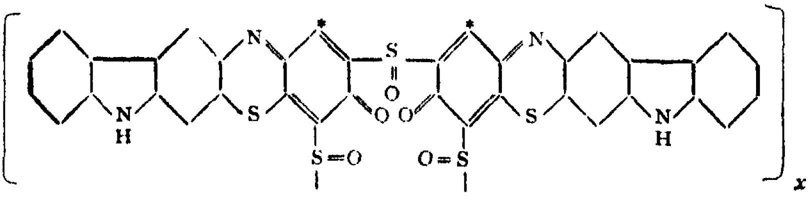
The main contribution to the chemistry of sulphur dyes and sulphurised vat dyes is due to Fierz-David and his collaborators[6, 7] who have collected valuable data regarding the type of linkages and ring systems occurring in sulphur dyes, especially in the blue and green series. Fierz-David formulated a scheme for the purification of these dyes, the impurities being removed by exhaustive extraction successively with dilute hydrochloric acid, dilute ammonia, water, alcohol and ether. Several blue and green dyes obtained by the sulphurisation of indophenols from diphenylamine (Pyrogen Indigo), dimethylaniline (Immedial Pure Blue), carbazole (Hydron Blue), 1-phenylaminonaphthalene-8-sulphonic acid (Pyrogen Green), etc., were thus purified.



Immedial Pure Blue (III)



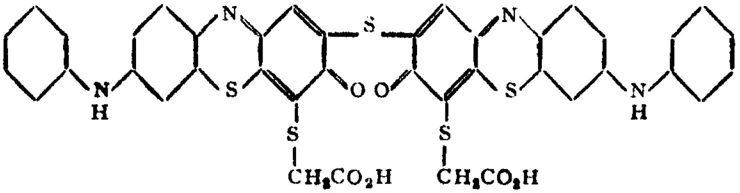
Pyrogen Indigo (IV)



Hydron Blue (V)

In spite of the inevitable limitations of this method of purification, and although important data, such as the molecular weight, could not be determined, Fierz-David was able to suggest structures for these dyes (*e.g.*, Immedial Pure Blue; Pyrogen Indigo; Hydron Blue) which explain most of their known properties. The thiazine units in these dyes were estimated by sulphonating the dyes with a mixture of concentrated sulphuric acid and chlorosulphonic acid to make them water-soluble, and then titrating them with titanous chloride.[7] The possibility of decomposition of the dyes during the acid treatment and the recorded results of the titrations indicated the limited value of the method.

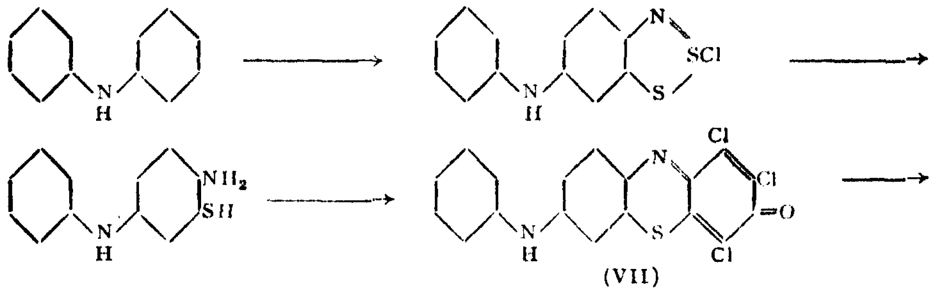
The solubility of the Immedial Pure Blue type of dye in aqueous sodium sulphide is attributed by Fierz-David[7] to the reduction of the quinonimine groups and to the fission of the disulphoxide groups to the thiols. The yellow solution obtained by alkaline reduction gave on air-oxidation a blue solution which was stable in the cold for a very long time. This behaviour distinguishes these sulphur dyes from the sulphurised vat dyes which are soluble as leuco-derivatives only in the presence of alkaline hydrosulphite and are precipitated in the quinonoid form by air-oxidation. In the case of sulphur dyes mild oxidation by air causes the re-formation of the quinonimine groups, but the thiol groups formed in the reduction remain unaffected under these conditions and impart alkali solubility to the dye. On boiling or acidification re-oxidation of the thiols to the insoluble disulphides occurs, resulting in the precipitation of the dye from the blue solution. The leuco-compounds from Pyrogen Indigo and Hydron Blue were condensed with chloracetic acid to form alkali-soluble derivatives which, however, were very unstable to air-oxidation. By carefully working in absence of air Bernasconi and Fierz-David[6] successfully isolated and purified the derivative from Pyrogen Indigo, for which the structure (VI) has been assigned on



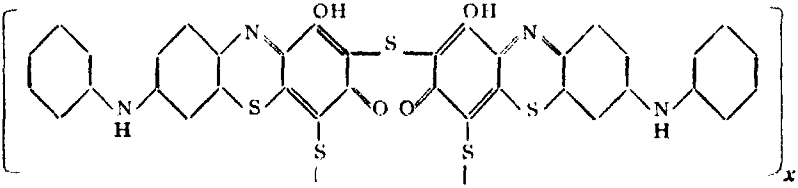
(VI)

the basis of elementary analysis. The formation of the thioglycollic acid derivatives was considered as a further proof of disulphide or disulphoxide linkages in the molecule of Pyrogen Indigo and its analogues. Considering the possibility of the phenolic hydroxyls in the leuco-derivatives also (or in fact in preference to the thiol groups) reacting with chloracetic acid, and the instability of the derivatives as being due to the ready fission of O-carboxymethyl ($-OCH_2CO_2H$) on account of the great tendency for the re-formation of thiazones by air-oxidation, it is necessary to interpret the results of Bernasconi and Fierz-David[6] with caution.

The problem of the constitution of sulphurised indophenol dyes was then approached from the synthetic angle. Employing the Herz synthesis,[8] Fierz-David[7] synthesised (VIII), which was very similar to Pyrogen Indigo by the following scheme:

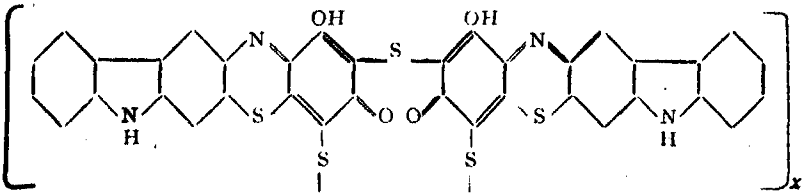


(VII)



(VIII)

On similar grounds synthetic equivalent of Hydron Blue was formulated as (IX):



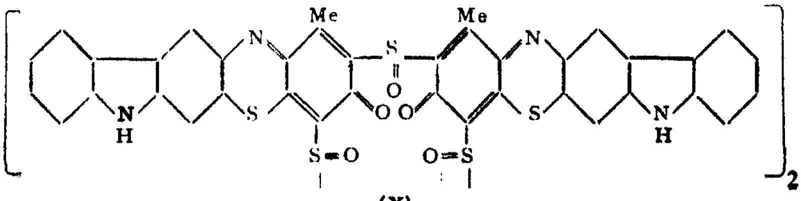
(IX)

Employing trichlorotoluquinone and dichloro-*p*-xyloquinone in place of chloranil, Fierz-David[7] observed that the product in the first case had poor tinctorial power, while the latter did not behave as a sulphide or sulphurised vat dye. This proved that at least one of the important sulphur containing groups must be in the *o*-position to the thiazine ring. On the basis of these results and elementary analysis the structures (VIII) and (IX) were suggested for synthetic Pyrogen Indigo and Hydron Blue, and (IV) and (V) respectively for the purified commercial dyes.

Bernasconi and Fierz-David[6] have formulated the synthetic analogue (VIII) of Pyrogen Indigo as a hydroxylated derivative containing one hydroxyl group per benzothiazine unit and the sulphur links as sulphide and disulphide links as against sulphoxide and disulphoxide linkages in the commercial dyes without giving any evidence barring elementary analysis. Shibata and Nishi[6] have also supported the phenolic structure for synthetic Hydron Blue on the basis of elementary analysis. Fierz-David[7, 10] however has sometimes assumed the complete identity of the synthetic dyes with the commercial analogues prepared by a thionation process, and on other occasions he has merely marked the positions in question with asterisks.[10] In one case[7] he has formulated a carbon-carbon linkage between pairs of dibenzothiazine units in a black dye obtained by intense thionation of a sulphur dye prepared from *p*-anisidine. Considering that no proof as regards the presence of the hydroxyl groups in (VIII) and (IX) is available, and secondly the very close resemblance in the elementary analysis of the purified commercial dyes and their synthetic analogues[6, 9] (the molecular formulæ of V and IX differ only in the latter having one oxygen atom less), there appears to be no reason for differentiating between the commercial and synthetic dyes. In support of this view may be cited the observation of Bernasconi and Fierz-David[6] that the two are very similar and give similar absorption spectra.

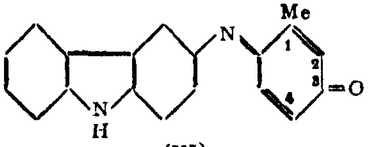
The constitution (V) for Hydron Blue can be valid only if *x* stands for 2, or if polymerisation has taken place by a carbon-carbon linkage at the position marked *. The latter possibility is unlikely on the assumption that Hydron Blue (V) and Immedial Pure Blue (III) are similarly constituted, since the latter on bromination gave (I).[4] We have now desulphurised Hydron Blue by treatment with Raney nickel in morpholine solution and obtained a product, which is identical with the reduction product from carbazole-indophenol, thus providing further and more definite proof of the absence of carbon-carbon linkages between the thionated carbazole indophenol units.

If Hydron Blue was a dimer ($x = 2$ in V), a compound such as (X) should be similar to Hydron Blue in its dyeing and other properties. Carba-



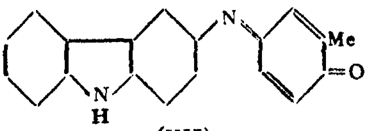
(X)

zole was condensed with nitroso-*m*-cresol, and the indophenol (XI) was thionated when a dye presumably of the structure (X) was obtained. This product, however, gave a weak greyish blue shade, indicating the importance of polymerisation through the positions occupied by the methyl groups for the dyeing property associated with Hydron Blue. Fierz-David[7] had also observed the poor tinctorial power of the dye from methyldichloro-thiazone obtained by the condensation of mercaptoaminocarbazole and trichloro-toluquinone, but since the methyldichloro-thiazone can have three alternative structures, sulphurisation can take place in three different ways. When, however, (XI) is thionated, cyclisation to the thiazine must take place in the 5-position, and further sulphurisation can only proceed through the 2 and 4 positions leading to (X) or a similar structure. The poor dyeing property of (X) thus provides definite proof that x must be more than two in structure (V) and that the 1-position must be involved in the polymerisation. If the structure (IX) for synthetic Hydron Blue were correct, (IX) and (X) should have similar dyeing properties, while in actual fact (X) had poor tinctorial power. This indicates that synthetic Hydron Blue is not a phenolic derivative such as (IX), as suggested by Fierz-David,[6] but is essentially identical with the commercial dye.

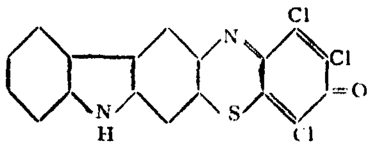


(XI)

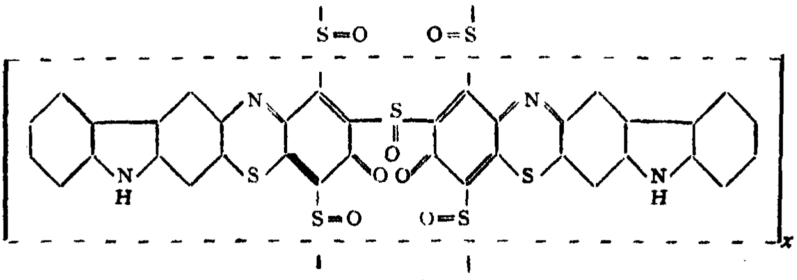
In order to establish other sites of polymerisation, the indophenol (XII), from nitroso-*o*-cresol and carbazole, was thionated. The resulting product



(XII)



(XIV)



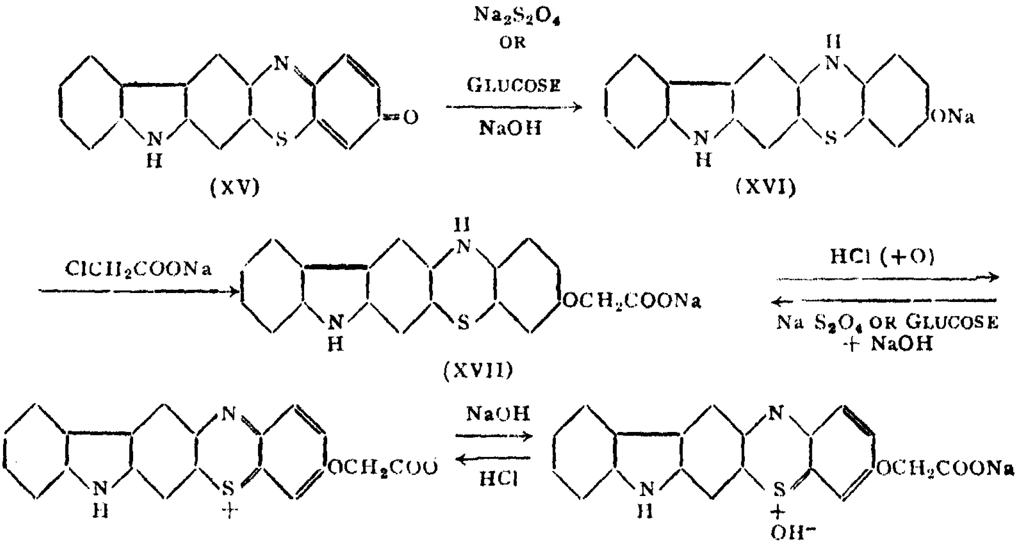
(XIII)

gave a weak grey shade, indicating that polymerisation through at least one of the positions *ortho* to the carbonyl group in the thiazones is fundamental to the dyeing property of Hydron Blue.

Taking all these facts into consideration, the constitution (XIII) is now proposed for Hydron Blue. This differs from the structure (V) suggested by Fierz-David with regard to the manner in which the thiazine from carbazole-indophenol polymerises to give Hydron Blue. Fierz-David suggested polymerisation through disulphoxide linkages, but it has been pointed out earlier that such a structure does not allow polymerisation beyond the tetrameric stage ($x = 2$ in V), and does not take into account polymerisation at the 1 : 1′ positions. The constitution now suggested postulates polymerisation through sulphoxide linkages. Other analogous sulphurised indophenols such as Immedial Pure Blue and Pyrogen Indigo can also be similarly constituted as units polymerising through sulphoxide groups.

It is well known that when chlorinated intermediates are thionated the halogen is generally replaced by sulphur; under suitable conditions of thionation each chlorine atom can be replaced by a thiol group, so that this provides a useful method for locating the position of the latter. It is therefore likely that when the trichlrothiazone (XIV), obtained by Herz synthesis, is thionated all the halogen atoms are replaced by sulphur linkages leading to (XIII), as this is the only structure possible which will agree with the sulphur content of Hydron Blue. The preparation of the 1 : 3 : 6 : 8-tetrabromo-derivative (I) from Immedial Pure Blue suggests substitution in the 1 : 3-positions by sulphur linkages, which are split off and replaced by bromine during bromination of the dye. The apparent anomaly of the absence of a bromine atom in the 4-position in (I) in place of a sulphur linkage in the parent dye, may be due to the lability of bromine in this position. In this connection it may be mentioned that Fierz-David[7] found that trichlorothiazones of the type of (XIV) could not be isolated in an analytically pure condition due to the lability of one of the chlorine atoms, probably that substituted in the 4-position.

Frank[11] has prepared a thioglycollic acid from Immedial Indone, which on oxidation gave a blue dye; the thioglycollic acid linkage remaining unaffected during this oxidation. The instability of the thioglycollic acid derivatives such as (VI) to air-oxidation noted by Fierz-David[7] cannot thus be readily explained. The formation of these derivatives from Hydron Blue and other analogous dyes represented by the structure (XIII) is due to the reaction of chloracetic acid with the phenolic hydroxyls of the leuco-compounds, giving glycollic instead of thioglycollic acid derivatives as suggested by Fierz-David. When these derivatives are exposed to air the thiazones are readily re-formed with fission of the carboxymethyl groups; the great instability of these derivatives to air-oxidation is thus accounted for. As an experimental proof of the formation of the diglycollic acid derivative from the unit (XIII) of Hydron Blue by the interaction of the phenolic groups of the leuco-compound with chloracetic acid, the glycollic acid from the leuco-derivative (XVI) of the simple thiazone (XV) was prepared. Condensation of the leuco-compound (XVI) with sodium chloracetate under weakly alkaline conditions, followed by acidification, gave a blue precipitate of the glycollic acid derivative (XVIII). As this product (XVIII)

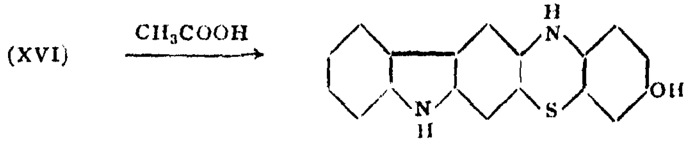


(XV) (XVI)

(XVII)

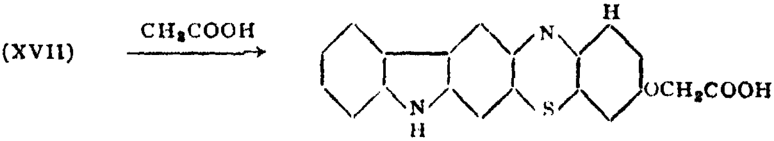
(XVIII) (XIX)

$$(XV) \xrightarrow{NaOH + Na_2S_2O_4} (XVI)$$



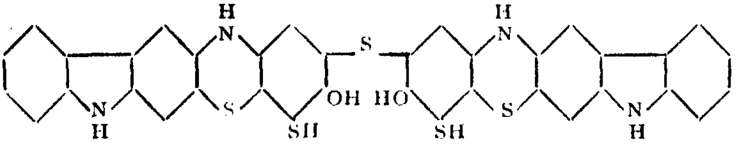
(XX)

$$(XVIII) \xrightarrow{NaOH + Na_2S_2O_4} (XVII)$$



(XXI)

is slowly oxidised by air under acid conditions to the parent thiazone (XV), it was worked up in an atmosphere of carbon dioxide. The glycollic acid dissolves in aqueous sodium hydroxide giving a violet blue solution from which the glycollic acid can be reprecipitated by acidification. On reduction with glucose and alkali, (XVIII) gave a pale grey vat (XVII) from which it can be regenerated by air oxidation or acidification. On the other hand, the vat (XVII), obtained by treatment of (XVIII) with alkaline hydrosulphite, when acidified gave the acid vat (XXI) as a yellowish olive precipitate. The thiazone (XV) also behaved similarly giving an olive acid vat (XX) on acidification of the alkaline hydrosulphite vat, and giving the parent thiazone (XV) on acidification of the alkaline glucose vat. The deep blue colour of the glycollic acid and of its solution in aqueous alkali can be accounted for by constituting the glycollic acid as (XVIII) and (XIX) under acid and alkaline conditions. It may be mentioned that the blue glycollic acid obtained by Frank[11] from Immedial Indone, referred to earlier, has been assigned a constitution similar to (XVIII). While the thiazone (XV) dyes a bright reddish blue shade on cotton from an alkaline hydrosulphite vat which is fast to soaping, the glycollic acid (XVIII) is non-substantive. The latter (XVIII) is further distinguished from the thiazone (XV) by the fact that it dyes a purple shade on wool when dyed as an acid dye. The formation of the glycollic acid (XVIII) from the thiazone (XV) provides experimental evidence for the suggestion that in Hydron Blue also similar derivatives are formed, and not the thioglycollic acid derivatives as proposed by Fierz-David.[6] If thiols are formed during the reduction of Hydron Blue (V) to the leuco-derivative, reaction of the latter with chloroacetic acid should yield a tetra-acetic acid derivative, corresponding to the two thiol and the two phenolic groups in (XXII) as against the di-acetic acid derivative (VI) obtained by Fierz-David[6] in the case of the analogous dye, Pyrogen Indigo. It appears, therefore, that the chloracetic acid reaction product of Fierz-David is a diglycollic acid derivative of the type (XVIII).


(XXII)

The solubility of Hydron Blue and analogous dyes after air-oxidation of the leuco derivatives of these dyes, which was explained by Fierz-David on the basis of disulphide or disulphoxide linkages, cannot be readily accounted for if the structure such as (XIII) is postulated for these dyes. In view of the ready oxidation of thiols in alkaline solution by air, the stability of the sodium thiophenolates noted by Fierz-David[7] is indeed surprising. When Hydron Blue is reduced by sodium sulphide it gives a green vat from which cotton can be dyed to give a dull blue shade. It appears in Hydron Blue (XIII), the quinoneimine groups are progressively reduced, the final stage of reduction being the pale yellow vat obtained by treatment with alkaline hydrosulphite. The green vat obtained on treatment with sodium sulphide and the blue solution obtained after air-oxidation may represent intermediate stages in oxidation in which only part of the quinoneimine groups in the polymeric structure (XIII) are regenerated, while others remain reduced as phenolic groups giving alkali-solubility. The sulphurised vat dyes such as Hydron Blue are distinguished from the sulphide dyes such as Immedial Pure Blue and Pyrogen Indigo by their greater fastness, insolubility or sparing solubility in sodium sulphide and by their being dyed from an alkaline hydrosulphite vat. Since all these dyes are now regarded as possessing the same structural pattern as represented by (XIII), the differences in solubility in sodium sulphide may be due to the decreased solubility on account of the presence of carbazole units in Hydron Blue as against *p*-dimethylamino and *p*-phenylamino groups which are present in Immedial Pure Blue and Pyrogen Indigo respectively.

EXPERIMENTAL

Preparation of carbazole-indophenols.—Carbazole (10 g.) was dissolved in concentrated sulphuric acid (250 c.c.) and cooled to − 13°. A soluiton of *p*-nitrosophenol (7·5 g.) in concentrated sulphuric acid (75 c.c.) was also cooled to − 13°, and then added rapidly to the above solution under vigorous stirring when the temperature rose to − 4 to − 5°. The solution was further worked up under cooling till the temperature was again − 13° (5–10 minutes) and was then poured over ice. The indophenol which separated was washed, dried in vacuum (15 g.), and then purified by dissolving in acetone and reprecipitation with water when it separated as a finely divided precipitate. (Found: N, 10·0. $C_{18}H_{12}ON_2$ requires N, 10·2%.) Carbazole-indophenol gave a light brown suspension in aqueous sodium sulphide and a colourless colloidal alkaline hydrosulphite vat. It is non-substantive to cotton.

Indophenols (XII) and (XI) from carbazole *p*-nitroso-*o*-cresol and *p*-nitroso-*m*-cresol were similarly prepared. (Found: for XI N, 10·2, and for XII N, 10·0. $C_{19}H_{14}ON_2$ requires N, 10·0%.)

Thionation of carbazole-indophenols.—Hydron Blue R was prepared by heating carbazole-indophenol (3·6 g.), fused sodium sulphide (3·4 g.), sulphur (4·32 g.), and butanol (25 c.c.) under reflux with mechanical agitation for 48 hours. After distilling the solvent, the melt was diluted with sodium chloride solution and the excess of sulphur was removed from the crude dye by extraction with aqueous sodium suphide (yield, 5 g.). Thionation of the indophenols (XI) and (XII) was similarly carried out to give the corresponding dyes.

The thionated dyes were purified according to Fierz-David[7] by washing with water and then extracting successively with alcohol, ether and carbon disulphide in a soxhlet. The nitrogen content of the purified Hydron Blue is in agreement with the constitution (XIII). (Found: N, 7·2. $C_{36}H_{16}O_6N_4S_5$ requires N, 7·5%), but the analysis of the purified dyes from (XI) and (XII) could not be related to any definite structure.

The dyeing properties of the purified dyes were then compared. Hydron Blue R had good substantivity to cotton, practically all the dye being exhausted at the end of the dyeing (3% shade), and very little bleeding was observed in soaping. Thionated *m*-cresol indophenol (XI) was less substantive than Hydron Blue and dyed a pale blue shade, which bled considerably in soaping. The purified thionated dye from (XII) had little or no dyeing property, but the crude product gave a brownish black shade inferior in tinctorial power as compared to Hydron Blue. The dyeings were again not fast to soaping. Hydron Blue R also dyes a deep blue shade on cotton from sodium sulphide vat.

Raney nickel reduction of carbazole-indophenol.—Pure carbazole-indophenol (2 g.), Raney nickel (20 g.) and morpholine (50 c.c.) were refluxed under stirring for 8 hours. The blue solution turned yellow on reduction. The reaction mixture was filtered and the nickel residue was washed twice with hot morpholine. The total morpholine extracts were poured into a mixture of ice and hydrochloric acid. The precipitate obtained was filtered and washed till free from hydrochloric acid, dried (1·5 g.), and finally purified by dissolving in acetone and precipitating by water. The reduced bluish violet product was collected and dried in vacuum, m.p. 220–2°. (Found: N, 10·0. $C_{18}H_6ON_2$ requires N, 10·1%.) The parent carbazole-indophenol does not possess a sharp m.p.

Raney nickel reduction of Hydron Blue R.—Hydron Blue R, purified according to Fierz-David,[7] (1 g.), Raney nickel (10 g.) and morpholine (50 c.c.) were refluxed for 8 hours. The reduction product was found to be free from sulphur and was isolated as above (yield, 0·4 g.). After purification from acetone, it melted at 218–220°; undepressed when mixed with the reduction product from carbazole-indophenol (Found: N, 10·1%).

Preparation of the thiazone (*XV*).—The thiazone was prepared according to Kulikov.[12] A solution of carbazole-indophenol (1 g.) in acetic acid (8 c.c. of 80%) and alcohol (500 c.c.) was treated with 0·05 N sodium thiosulphate solution till the violet colour disappeared. The solution was filtered and the leuco-indophenol thiosulphate obtained was oxidised by the addition of a solution of sodium acetate (1·5 g.) and ferric chloride (18 c.c. of 50%). After leaving the mixture overnight the precipitate of the thiazone (XV) separated. The thiazone is sparingly soluble in aqueous sodium hydroxide, and gives a pale yellow vat in alkaline hydrosulphite from which cotton is dyed a bright blue shade. On acidification of the alkaline hydrosulphite vat with acetic acid an olive precipitate of the acid vat (XX) separated. The thiazone is not reduced in alkaline glucose solution at room temperature, but on warming it gives a vat from which the thiazone could be regenerated by acidification with acetic acid.

Preparation of the glycollic acid (*XVIII*).—The above thiazone (0·62 g.), glucose (2·17 g.) and 5% sodium hydroxide solution (30 c.c.) were boiled together till the thiazone was reduced. The volume was then made to 120 c.c. with water and the solution was heated to boil. A solution of chloracetic acid (1·86 g.) in 5% sodium hydroxide (16 c.c.) was then added and the solution was heated on water-bath for an hour. The unconverted thiazone was removed by filtration and the filtrate was cooled to 0–5°, acidified with 5% hydrochloric acid (Congo Red) and then transferred to a 250 c.c. stoppered measuring cylinder. The air in the cylinder was displaced by carbon dioxide and the precipitated glycollic acid allowed to settle at 5–10°. The supernatant pale greenish yellow solution was decanted off, the glycollic acid was shaken with water and again allowed to settle after covering with carbon dioxide. The glycollic acid was further washed thrice in a similar manner and then filtered under a current of carbon dioxide and washed with water. It was dissolved in cold 5% sodium hydroxide solution (50 c.c.) when a greenish blue solution was obtained. After filtration the alkaline solution was acidified with dilute hydrochloric acid and the blue precipitate of the glycollic acid (XVIII) was cooled to 10°, filtered under carbon dioxide, washed till neutral and finally dried over phosphorous pentoxide in vacuum. The dry blue powder of the glycollic acid decomposed above 230°. The glycollic acid (XVIII) gives a purple solution in aqueous sodium bicarbonate and a violet blue solution in aqueous sodium hydroxide from which it can be recovered as a blue precipitate on acidification. On warming with alkaline glucose solution, it gave a pale grey vat from which the acid can be recovered by acidification with acetic acid. Alkaline hydrosulphite reduces the acid (XVIII) to a pale grey vat in the cold and acidification of the reduced solution gives a yellowish olive precipitate of the acid vat, presumably of the reduced glycollic acid (XXI). When wool is dyed first from a weak sodium bicarbonate and then an acetic solution of the glycollic acid (XVIII), a purple shade is obtained. The glycollic acid did not possess affinity to cotton as a vat dye.

SUMMARY

The constitution (V) proposed by Fierz-David for Hydron Blue, in which polymerisation of the thiazine from carbazole-indophenol through disulphoxide linkages is postulated, does not take into account the necessity of polymerisation through the positions marked by asterisks in (V) to account for the dyeing property of Hydron Blue. The fact that polymerisation of thionated carbazole-indophenol units does not proceed through carbon-carbon linkages has been proved by the identity of the reduction products from carbazole-indophenol and from Hydron Blue, obtained by treatment with Raney nickel. The formation of the glycollic acid (XVIII) from the thiazone (XV) indicates the possibility of reaction between the phenolic groups in leuco-Hydron Blue and chloracetic acid. If disulphoxide linkages were present in Hydron Blue (V) and its analogues, such as Pyrogen Indigo (IV), the condensation of their leuco-derivatives with chloracetic acid should have given tetra-acetic acid derivatives corresponding to the two thiol and the two phenolic groups in their leuco-compounds (*e.g.*, XXII). Fierz-David, however, obtained a diacetic acid derivative from Pyrogen Indigo. Taking these facts into consideration, the constitution (XIII) is now proposed for Hydron Blue, in which polymerisation of thionated carbazole-indophenol units through sulphoxide linkages is postulated. Other analogous sulphurised indophenols can also be similarly constituted. The new constitution for sulphurised indophenol dyes readily accounts for the formation of a diacetic acid derivative from Pyrogen Indigo on the basis of the reaction between chloracetic acid and the phenolic groups in leuco-Pyrogen Indigo as in the case of the simple thiazone (XV).

We are indebted to the Council of Scientific and Industrial Research under whose auspices part of the work was carried out, and to Mr. T. S. Gore for the microanalyses recorded in the paper.

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CHALKONES: PREPARATION OF SOME HYDROXY-CHALKONES, THEIR BROMINATION AND STUDY OF THE REACTIVITY OF THE BROMO DERIVATIVES

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THE Chalkones were prepared according to the method of Sorge.[1] The bromination of these chalkones gave bromo derivatives, but in the case of dihydroxy compounds, it was observed that the nucleus containing -OH groups was more reactive than the double bond in the molecule.

The reactivity of these dibromide derivatives was examined with potassium iodide, potassium hydroxide, sodium alkoxide, pyridine and potassium cyanide.

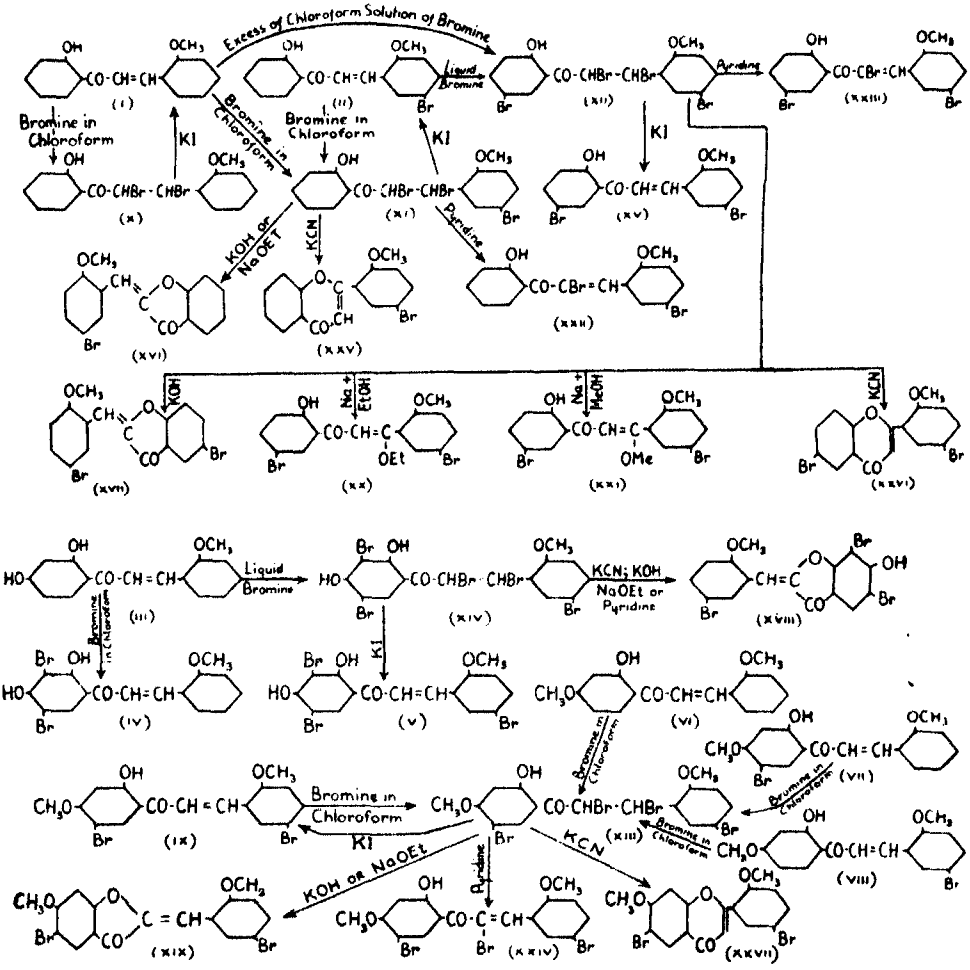
With potassium iodide both bromine atoms of the dibromide were found labile, when the corresponding styryl ketones were obtained, whose constitutions were proved by mixed melting points with authentic specimens. (*cf.* Dodwadmath and Wheeler[2]; Barne and Payton[3]; Nadkarni, Warrior and Wheeler[4]).

With potassium hydroxide these dibromides gave benzylidene coumaranones. Similar results were obtained with sodium alkoxide, except in the case of the ketone (XII) when β-alkoxy-styryl ketones were obtained, thus pointing to the more reactive nature of the β bromine atom (*cf.* Cullinane and Phillipott[5]; Kõlher and Addinall[6]; Price and Bogert[7]; Nadkarni, Warrior and Wheeler[4]; Bhagwat and Wheeler[8]; Rao and Wheeler[9]).

With Pyridine ketones (XI), (XII) and (XIII) gave α-bromostyryl ketones (XXII), (XXIII) and (XXIV) respectively whilst the ketone (XIV) gave the coumaranone (XVIII) (*cf.* Nadkarni, Warrior and Wheeler[4]; Bhagwat and Wheeler[8]; Rao and Wheeler[9]).

Potassium cyanide gave flavones (XXV), (XXVI) and XXVII) in the case of ketones (XI), (XII) and (XIII) respectively, whilst ketone (XIV) gave the coumaranone (XVIII) (*cf.* Hutchins and Wheeler[10]; Rao and Wheeler[9]).

DIAGRAMMATIC PRESENTATION OF RESULTS OF CHALKONES BY H.P.VANDREWALA AND G.V.JADHAV.



These results point out that the reactivity of the bromine atoms depend upon the nature of the reagent as well as on the substituents in the phenyl part of the ketone molecule. With more basic reagents β-bromine atom is more reactive than the α-one.

EXPERIMENTAL.

The chalkones were prepared by dissolving the requisite ketone and aldehyde in alcohol and a strong caustic potash solution at ordinary temperature. The mixture, after a suitable period, was diluted with water, alkali neutralised and crystallised from a suitable solvent. The compounds are described in Table I.

TABLE I

Name of Chalkone	Name in Quantity of Ketone	Name and Quantity of aldehyde	Quantity of KOH	Time	Solvent	Cryst. Shape	m.p.	Found %	Formula requires %
2-Hydroxyphenyl-β-2′-methoxystyryl ketone (I)	O-Hydroxyacetophenone (20 g.)	O-Methoxybenzaldehyde (20 g.)	40 g. in 60 c.c.	Over night	Alcohol	Yellow needles	110–11°	C. 75·2; H, 5·8	$C_{16}H_{14}O_3$ requires C, 75·6; H, 5·6
2-Hydroxyphenyl β-2′-methoxy-5′-bromostyryl ketone (II)	O-Hydroxyacetophenone (2 g.)	2-Methoxy-5-bromobenzaldehyde (3·5 g.)	6 g. in 8 c.c.	do	Acetic acid	do	120–21°	Br, 24·4	$C_{16}H_{13}O_3$ Br requires Br, 24·3
2:4-Dihydroxyphenyl β-2′-methoxystyryl ketone (III)	Resacetaphenone (20 g.)	O-Methoxybenzaldehyde (18 g.)	60 g. in 80 c.c.	48 hrs.	Acetic acid	do	191–92°	C, 70·8; H, 5·4	$C_{16}H_{14}O_4$ requires C, 71·1; H 5·2
2:4-Dihydroxy-3:5-dibromophenyl-β-2′-methoxystyryl ketone (IV)*	3:5-Dibromoresacetophenone (2 g.)	O-Methoxybenzaldehyde (1·5 g.)	6 g. in 8 c.c.	48 hrs.	Acetic acid	do	168–69°	Br, 37·8	$C_{16}H_{12}O_4Br_2$ requires Br, 37·4
2:4-Dihydroxy-3:5 dibromophenyl-β-2′-methoxy-5′-bromostyryl ketone (V)†	3:5-Dibromoresacetophenone (2 g.)	2-Methoxy-5-bromobenzaldehyde (1·5 g.)	6 g. in 8 c.c.	24 hrs.	do	do	194–95°	Br, 47·1	$C_{16}H_{11}O_4Br_3$ requires Br, 47·3
2-Hydroxy-4-methoxyphenyl-β-2′-merhoxystyryl ketone (VI)	Peanol (10 g.)	O-Methoxybenzaldehyde (8 g.)	20 g. in 30 c.c.	24 hrs.	Alcohol	do	93–94°	C, 71·5; H, 5·8	$C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6
2-Hydroxy-4-methoxy-5-bromophenyl-β-2′-methoxystyryl ketone (VII)	5-Bromopeanol	do	do	do	Acetic acid	do	158–59°	Br, 22·1	$C_{17}H_{15}O_4Br$, requires Br 22
2-Hydroxy-4 methoxyphenyl β 2′-methoxy-5′-bromostyryl ketone (VIII)	Peanol	2-Methoxy-5 bromobenzaldehyde	do	do	do	do	127–28°	Br, 21·6	$C_{17}H_{15}O_4$ Br requires Br 22
2 Hydroxy-4-methoxy-5-bromophenyl β-2′-methoxy-5-bromostyryl ketone (IX)	5-Bromopeanol	2-Methoxy-5-bromobenzaldehyde	do	do	do	do	191–92°	Br, 36·6	$C_{17}H_{14}O_4Br_2$ requires Br, 36·2

(*) This was also obtained by boiling for 5 hours ketone (III) (3 g.) in chloroform (300 c.c.) and leaving the reaction mixture overnight at room temperature.

(†) This was also obtained by boiling under reflux ketone (XIV) with alcoholic potassium iodide solution.

The bromination of these chalkones was carried in chloroform medium with 10 per cent. solution of bromine in chloroform and the bromo derivatives were obtained after the removal of the solvent and crystallised from a suitable solvent. The compounds are described in Table II. When liquid bromine was used for bromination, the solid was washed with sodium bisulphite before crystallisation.

Action of potassium iodide

The ketone (X) was dissolved in acetone (40 c.c.) and potassium iodide (1 g.) was added to it. The mixture was then boiled under reflux for about 45 minutes. The solid obtained after the removal of the solvent was washed with sodium thiosulphate solution and finally crystallised from alcohol in yellow needles, m.p. 110–11°. It was found identical with (I) by mixed melting point.

The ketone (XI) under similar conditions gave ketone (II). The ketone (XII) when refluxed with potassium iodide in acetone solution for two hours gave *2-hydroxy-5-bromophenyl β-2′-methoxy-5′-bromostyryl ketone (XV)*. It crystallised from acetic acid in yellow needles, m.p. 156–57°. Found: Br, 38·6, $C_{16}H_{12}O_3$ Br_2 requires Br, 38·8 per cent.

The ketone (XIV) under similar conditions gave ketone (V) and ketone (XIII) gave the ketone (IX).

Action of potassium hydroxide

The ketone (XI) (2 g.) was dissolved in acetone (500 c.c.), 10 per cent. solution of caustic potash (20 c.c.) was added to it and the mixture boiled under reflux for about five minutes. The solid obtained on cooling was washed with water and finally crystallised from alcohol in yellow needles, m.p. 161–62°. It gave red colour with sulphuric acid. Found: Br, 24·6, $C_{16}H_{11}O_3Br$ requires Br, 24·2 per cent. It should be 2′-methoxy-5′-bromobenzylidene coumaranone (XVI).

Ketone (XII) under similar conditions gave *5-bromo-2′-methoxy-5′ bromobenzylidene coumaranone (XVII)*. It crystallised from acetic acid in yellow needles, m.p. 173–74°. It gave red colour with sulphuric acid. Found: Br, 39·2, $C_{16}H_{10}O_3$ Br_2 requires Br, 39·02 per cent.

Ketone (XIV) under similar condition gave 5: 7 *dibromo-6-hydroxy-2′-methoxy-5′-bromobenzylidene coumaranone* (XVIII). It crystallised from a mixture of acetic acid and nitrobenzene in yellow needles, m.p. 298–99°. Found: Br, 47·2; $C_{16}H_9O_4Br_3$ requires Br, 47·5 per cent. It gave red colour with sulphuric acid.

TABLE II

Name of the Ketone	Vol. of chloroform	Amount of bromine solution	No. from Table I and quantity of ketone used	Temp. of reaction and time	Colour and shape of crystal	Solvent	m.p.	Found %	Formula requires %
2-Hydroxyphenyl α-β-dibromo-β-2′-methoxy-phenyl ethyl ketone **(X)**	25 c.c.	35 c.c.	(I), 5 g.	10–15°; 1 hr.	Yellow plates	Chloroform and petroleum ether	162–63°	Br, 38·9	$C_{16}H_{14}O_3Br_2$ requires Br, 38·7
2-Hydroxyphenyl-α-β-dibromo-β-2′-methoxy-5′-bromophenyl ethyl ketone (XI)	(i) 25 c.c. (ii) 10 c.c.	70 c c. 12 c.c.	(I), 5 g. (II), 2 g.	Room Temp. 4 hrs. 10°, I hr.	Yellow needles do	Acetic acid and nitrobenzene do	178–79°	Br, 48·8	$C_{16}H_{13}O_3Br_3$ requires Br, 48·7
2-Hydroxy-5-bromophenyl-α-β-dibromo-β-2′-methoxy-5′-bromo-phenyl ethylketone (XII)*	10 c.c.	2 g. (liquid bromine)	(II), 1 g.	Boiled for ½ hr. and left at room temp. for 24 hrs.	Yellow plates	do	225–26°	Br, 55·9	$C_{16}H_{12}O_{12}Br_4$ requires Br. 55·9
2-Hydroxy-4-methoxy-5-bromophenyl α-β-dibromo-β-2′-methoxy-5′-bromophenyl ethyl ketone (XIII)†	10 c.c.	14 c.c.	(IX) 1 g.	Room temp. 24 hr. after boiling for 1 hr.	Small yellow plate	Acetic acid	208–09°	Br, 53·3	$C_{17}H_{14}O_4Br_4$ requires Br. 53·2
2:4-Dihydroxy-3:5-dibromophenyl α-β-dibromo-β-2′-methoxy-5′-bromophenyl ethyl ketone **(XIV)**	..	Liquid bromine 36 g.	(III), 10 g.	Room temp. short time	Yellow plates	Acetic acid and nitrobenzene	219–20°	Br, 59·6	$C_{16}H_{11}O_4Br_5$ requires Br, 59·98

(*) This was also obtained from (I) by using a large excess of chloroform solution of bromine at room temperature.

(†) This was also obtained from (VI), (VII) & (VIII) by bromination in chloroform. solutions.

Ketone (XIII) under similar conditions gave *5-bromo-6-methoxy-2'-methoxy-5'-bromo-benzylidene coumaranone (XIX)*. It crystallised in yellow needles from acetic acid, m.p. 258–59°. Found: Br, 36·7; $C_{17}H_{12}O_4Br_2$ requires Br, 36·4 per cent. It gave red colour with sulphuric acid.

Action of sodium alkoxide

2-Hydroxy-5-bromo-phenyl-β-ethoxy-β-2'-methoxy-5'-bromo-styryl ketone (XX).—The ketone (XII) was boiled with metallic sodium and ethyl alcohol for about three hours and the solid obtained on cooling crystallised from acetic acid in yellow needles, m.p. 160–61°. Found: Br, 35·1; $C_{18}H_{16}O_4Br_2$ requires Br, 35·1 per cent.

2-Hydroxy-5-bromo-phenyl-β-methoxy-β-2'-methoxy-5'-bromostyryl ketone (XXI), was obtained from ketone (XII) when methyl alcohol was used in place of ethyl alcohol with metallic sodium, m.p. 174–75°. Found: Br, 36·5; $C_{17}H_{14}O_4Br_2$ requires Br, 36·2 per cent.

When, however, ketones (XI), (XIII) and (XIV) were treated with sodium ethoxide coumaranones (XVI), (XIX) and (XVIII) respectively.

Action of pyridine

2-Hydroxyphenyl α-bromo-β-2'-methoxy-5'-bromo-styryl ketone (XXII); The ketone (XI) (1 g.) was boiled with pyridine (5 c.c.) for about five minutes and then diluted with excess of alcohol. The solid separated was washed with hydrochloric acid and finally crystallised from alcohol, in yellow needles, m.p. 134–35°. Found: Br, 39·2; $C_{16}H_{12}O_3Br_2$ requires 38·8 per cent.

2-Hydroxy-5-bromo-phenyl α-bromo-β-2'-methoxy-5'-bromostyryl-ketone (XXIII) was obtained from ketone (XII) by treatment with pyridine and working up as above. It crystallised from acetic acid in yellow needles, m.p. 165–66°. Fund: Br, 48·4; $C_{16}H_{11}O_3Br_3$ requires Br, 48·9 per cent.

Ketone (XIII) under similar conditions gave *2-hydroxy-4-methoxy-5-bromo-α-bromo-β-2'-methoxy-5'-bromostyryl ketone (XXIV)* of m.p. 253–54°. Found: Br, 45·9; $C_{17}H_{13}O_4Br_3$ requires Br, 46·1 per cent.

Ketone (XIV), however, under similar conditions gave the coumaranone (XVIII) described before.

Action of potassium cyanide

2'-Methoxy-5'-bromo-flavone (XXV).—Ketone (XI) (2 g.) *n*-propyl alcohol (60 c.c.) and potassium cyanide (2 g. in 100 c.c. water) were boiled under reflux for about forty-five minutes. The product obtained after the removal of the solvent crystallised from alcohol in white needles, m.p. 162–63°. It gave yellow coloration with sulphuric acid. (Found: Br, 24·5; $C_{16}H_{11}O_3Br$, requires Br, 24·2 per cent.)

6-*Bromo-2′-methoxy-5′-bromo-flavone* (*XXVI*) was obtained from ketone (XII) by the interaction with potassium cyanide as above. It also gave yellow coloration with sulphuric acid. It crystallised from acetic acid in white needles, m.p. 173–74°. Found: Br, 39·2; $C_{16}H_{10}O_3Br_2$ requires Br, 39·02 per cent.

6-*Bromo-7-methoxy-2′-methoxy-5′-bromo-flavone* (*XXVII*) was similarly obtained from ketone (XIII), m.p. 260–61°. Found: Br, 36·7; $C_{17}H_{12}O_4Br_2$ requires Br, 36·4 per cent.

Ketone (XIV), however, when similarly treated gave the coumaranone (XVIII) already described.

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ON THE CONGRUENCES OF RIBAUCOUR

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Ribaucour congruences[1] are the congruences formed by lines through points on one surface parallel to the normals to another surface, the two surfaces corresponding with orthogonality of linear elements. The latter surface is called the director surface and the former one is the surface of reference. The object of this paper is to obtain several properties of Ribaucour congruences.

1. Suppose S_1 is the surface of reference, the co-ordinates of any point on it being (x_1, y_1, z_1) and S is the director surface, the co-ordinates of any point on it being (x, y, z)

then $$\Sigma\, dx \cdot dx_1 = 0^2$$

or $$\Sigma \frac{\partial x}{\partial u} \cdot \frac{\partial x_1}{\partial u} = 0; \quad \Sigma \frac{\partial x}{\partial v} \cdot \frac{\partial x_1}{\partial v} = 0; \quad \Sigma \frac{\partial x}{\partial u} \cdot \frac{\partial x_1}{\partial v} + \Sigma \frac{\partial x}{\partial v} \cdot \frac{\partial x_1}{\partial u} = 0 \tag{1·1}$$

let the last of these equations be replaced by

$$\Sigma \frac{\partial x}{\partial u} \cdot \frac{\partial x_1}{\partial v} = \phi \mathrm{H}; \quad \Sigma \frac{\partial x}{\partial v} \cdot \frac{\partial x_1}{\partial u} = -\phi \mathrm{H} \tag{1·2}$$

Then if X, Y, Z are the direction cosines of the normal to S; E, F, G, D, D′, D″ are the fundamental coefficients of the first and the second order and K is the total curvature of S,

$$\Sigma \mathrm{X} \frac{\partial x_1}{\partial u} = \frac{\mathrm{D}' \frac{\partial \phi}{\partial u} - \mathrm{D} \frac{\partial \phi}{\partial v}}{\mathrm{KH}}; \quad \Sigma \mathrm{X} \frac{\partial x_1}{\partial v} = \frac{\mathrm{D}'' \frac{\partial \phi}{\partial u} - \mathrm{D}' \frac{\partial \phi}{\partial v}}{\mathrm{KH}} \tag{1·3}$$

where

$$\frac{\partial x_1}{\partial u} = \frac{\mathrm{D}\left(\phi \frac{\partial \mathrm{X}}{\partial v} - \mathrm{X} \frac{\partial \phi}{\partial v}\right) - \mathrm{D}'\left(\phi \frac{\partial \mathrm{X}}{\partial u} - \mathrm{X} \frac{\partial \phi}{\partial u}\right)}{\mathrm{KH}} \tag{1·4}$$

and

$$\frac{\partial x_1}{\partial v} = \frac{\mathrm{D}'\left(\phi \frac{\partial \mathrm{X}}{\partial v} - \mathrm{X} \frac{\partial \phi}{\partial v}\right) - \mathrm{D}''\left(\phi \frac{\partial \mathrm{X}}{\partial u} - \mathrm{X} \frac{\partial \phi}{\partial u}\right)}{\mathrm{KH}} \tag{1·5}$$

and similar expressions for y_1 and z_1.

Hence for the congruence of lines parallel to the normals to S, the coefficients e, f, f', g of Kummer's form are given by

$$e \equiv \Sigma \frac{\partial x_1}{\partial u} \cdot \frac{\partial X}{\partial u} = (D\mathcal{F} - D'\mathcal{E}) \frac{\phi}{\mathcal{H}} \tag{1·6}$$

$$f \equiv \Sigma \frac{\partial x_1}{\partial v} \cdot \frac{\partial X}{\partial u} = (D'\mathcal{F} - D''\mathcal{E}) \frac{\phi}{\mathcal{H}} \tag{1·7}$$

$$f' \equiv \Sigma \frac{\partial x_1}{\partial u} \cdot \frac{\partial X}{\partial v} = (D\mathcal{G} - D'\mathcal{F}) \frac{\phi}{\mathcal{H}} \tag{1·8}$$

$$g \equiv \Sigma \frac{\partial x_1}{\partial v} \cdot \frac{\partial X}{\partial v} = (D'\mathcal{G} - D''\mathcal{F}) \frac{\phi}{\mathcal{H}} \tag{1·9}$$

where $\mathcal{E}$, $\mathcal{F}$, $\mathcal{G}$ are the fundamental coefficients of the first order of the spherical representation of S.

Solving the equations (1 · 6) and (1 · 8) and the equations (1 · 7) and (1 · 9) we get

$$D = \frac{\mathcal{E}f' - \mathcal{F}e}{\phi \mathcal{H}} \tag{1·10}$$

$$D' = \frac{\mathcal{E}g - \mathcal{F}f}{\phi\mathcal{H}} = \frac{\mathcal{F}f' - \mathcal{G}e}{\phi\mathcal{H}} \tag{1·11}$$

$$D'' = \frac{\mathcal{F}g - \mathcal{G}f}{\phi\mathcal{H}} \tag{1·12}$$

The asymptotic lines on the director surface are given by

$$D du^2 + 2D' \, du dv + D'' dv^2 = 0 \tag{1·13}$$

or using the equations (1 · 10), (1 · 11) and (1 · 12) we get[3]

$$(\mathcal{E}f' - \mathcal{F}e) du^2 + (\mathcal{E}g - \mathcal{G}e + \mathcal{F}f' - \mathcal{F}f) du dv + (\mathcal{F}g - \mathcal{G}f) dv^2 = 0 \tag{1·14}$$

But this is also the equation of developable surfaces through the line of the congruence. Hence the *developable surfaces through a line of the congruence of Ribaucour cut the director surface in asymptotic lines.*

The lines of curvature on the director surface are given by

$$(ED' - FD) du^2 + (ED'' - GD) du dv + (FD'' - GD') dv^2 = 0 \tag{1·15}$$

But

$$E = \frac{1}{\mathcal{H}^2} [\mathcal{G}D^2 - 2\mathcal{F}DD' + \mathcal{E}D'^2] \tag{1·16}$$

$$F = \frac{1}{\mathcal{H}^2} [\mathcal{G}DD' - \mathcal{F}DD'' - \mathcal{F}D'^2 + \mathcal{E}D'D''] \tag{1·17}$$

$$G = \frac{1}{\mathcal{H}^2} [\mathcal{G}D'^2 - 2\mathcal{F}D'D'' + \mathcal{E}D''^2] \tag{1·18}$$

Writing down these values of E, F, G in (1·15) we get

$$(\mathcal{F}D - \mathcal{E}D')\,du^2 + (\mathcal{G}D - \mathcal{E}D'')\,du\,dv + (\mathcal{G}D' - \mathcal{F}D'')\,dv^2 = 0 \quad (1\cdot 19)$$

Using the equations (1·6), (1·7), (1·8) and (1·9) equation (1·19) becomes

$$e\,du^2 + (f + f')\,du\,dv + g\,dv^2 = 0 \qquad (1\cdot 20)$$

As in a congruence of Ribaucour the surface of reference is a middle surface, the equation (1·20) is the equation of the surfaces of distribution.[4] Hence the *surfaces of distribution through a line of a congruence of Ribaucour cut the director surface in the lines of curvature.*

The equations of characteristic surfaces are given by[5]

$$\begin{vmatrix} \delta\,du + \delta'\,dv & \delta'\,du + \delta''\,dv \\ e\,du + \frac{1}{2}(f + f')\,dv & \frac{1}{2}(f + f')\,du + g\,dv \end{vmatrix} = 0 \qquad (1\cdot 21)$$

where δ, δ', δ'' are the coefficients of Sannia's second fundamental quadratic form. Using the equations (1·10), (1·11) and (1·12) we get

$$\begin{vmatrix} D\,du + D'\,dv & D'\,du + D''\,dv \\ e\,du + \frac{1}{2}(f + f')\,dv & \frac{1}{2}(f + f')\,du + g\,dv \end{vmatrix} = 0 \qquad (1\cdot 22)$$

With the help of equations (1·6), (1·7), (1·8) and (1·9) equation (1·22) becomes

$$\begin{vmatrix} D\,du + D'\,dv & D'\,du + D''\,dv \\ 2(D\mathcal{F} - D'\mathcal{E})\,du + (D\mathcal{G} - D''\mathcal{E})\,dv & (D\mathcal{G} - D''\mathcal{E})\,du + 2(D'\mathcal{G} - D''\mathcal{F})\,dv \end{vmatrix} = 0 \quad (1\cdot 23)$$

or from the equations (1·16), (1·17) or (1·18) equation (1·23) becomes

$$\begin{vmatrix} D\,du + D'\,dv & D'\,du + D''\,dv \\ 2(ED' - FD)\,du + (ED'' - GD)\,dv & (ED'' - GD)\,du + 2(FD'' - GD')\,dv \end{vmatrix} = 0 \quad (1\cdot 24)$$

But equation (1·24) is the equation of characteristic lines[6] of the director surface, hence *the characteristic surfaces of a congruence of Ribaucour cut the director surface in characteristic lines.*

Hence *the developable surfaces, surfaces of distribution and characteristic surfaces through a line of a congruence of Ribaucour cut the director surface in asymptotic lines, lines of curvature and characteristic lines respectively.*

From the above we see that if the spherical representations of developable surfaces, surfaces of distribution or characteristic surfaces are parametric, the spherical representations of asymptotic lines, lines of curvature or characteristic lines of director surface at the corresponding point are also parametric.

Hence *the spherical representations of developable surfaces, surfaces of distribution and characteristic surfaces through a line of the congruence of Ribaucour correspond to the spherical representations of asymptotic lines, lines of curvature and characteristic lines of the director surface at the corresponding point.*

It is to be noted that these three surfaces form a cycle in the sense that the central planes corresponding to any one of these three surfaces are the double planes of involution determined by the corresponding central planes of the other two,[7] also if $f = 0$ and $\phi = 0$ are the developable surfaces and surfaces of distribution, then the repeated applications of forming the Jacobian with these two forms lead to only these three surfaces. A corresponding result holds for the three families of curves of the director surface.

2. From the equation (1·14) we see that the developable surfaces are parametric if

$$\mathcal{E}f' - \mathcal{F}e = 0 \tag{2·1}$$

and

$$\mathcal{F}g - \mathcal{G}f = 0 \tag{2·2}$$

or from the equations (1·10) and (1·12) we get

$$D = D'' = 0 \tag{2·3}$$

Hence the equation (1·19) of the surfaces of distribution becomes

$$\mathcal{E}\,du^2 - \mathcal{G}\,dv^2 = 0 \tag{2·4}$$

Hence *the central planes for the spherical representation of the surfaces of distribution through a line of a rectilinear congruence of Ribaucour bisect the angles between the central planes of the spherical representations of developable surfaces.*

Also from the equation (1·21) we see that the characteristic surfaces are parametric if

$$\delta' = 0,\ f + f' = 0 \tag{2·5}$$

hence the equation (1·20) of the surfaces of distribution becomes

$$e\,du^2 + g\,dv^2 = 0 \tag{2·6}$$

In a congruence of Ribaucour the surface of reference is a middle surface

$$\therefore\quad e\mathcal{G} + g\mathcal{E} - \mathcal{F}(f + f') = 0 \tag{2·7}$$

With the help of equations (2·5) and (2·7) equation (2·6) becomes

$$\mathcal{E}\,du^2 - \mathcal{G}\,dv^2 = 0$$

Therefore *the central planes for the spherical representations of the surfaces of distribution through a line of a rectilinear congruence of Ribaucour*

bisect the angles between the central planes for the spherical representations of the characteristic surfaces also.

3. *Normal congruences of Ribaucour.*—We know that the necessary and sufficient condition for a normal rectilinear congruence is[8]

$$\mathcal{E}\delta'' + \mathcal{G}\delta - 2\mathcal{F}\delta' = 0 \tag{3·1}$$

With the help of equations (1·10), (1·11) and (1·12) equation (3·1) becomes

$$\mathcal{E}D'' + \mathcal{G}D - 2\mathcal{F}D' = 0 \tag{3·2}$$

Suppose the surfaces whose spherical representations are minimal lines are represented by the parametric curves on the unit sphere, then

$$\mathcal{E} = \mathcal{G} = 0 \tag{3·3}$$

With the help of equation (3·3) equation (3·2) becomes

$$D' = 0 \tag{3·4}$$

as the fundamental coefficients of the first and second order for the director surface are not proportional.

Hence *the necessary and sufficient condition that the congruence of Ribaucour be normal is that the surfaces whose spherical representations are minimal lines correspond to the conjugate systems at the corresponding points of the director surface.*

4. Let the parametric curves on the director surface of a normal rectilinear congruence be conjugate, then

$$D' = 0 \tag{4·1}$$

The equation (3·2) becomes with the help of equation (4·1)

$$\frac{D}{\mathcal{E}} = -\frac{D''}{\mathcal{G}} \tag{4·2}$$

Also the surfaces whose spherical representations on the unit sphere correspond to the parametric curves on the director surface have their parameters of distribution equal to

$$P_1 = \frac{\delta}{\mathcal{E}} = \frac{D}{\delta}\phi;\ P_2 = -\frac{\delta''}{\mathcal{G}} = -\frac{D''}{\mathcal{G}}\phi \tag{4·3}$$

Hence, *the two surfaces through a ray of a normal congruence of Ribaucour which correspond to the conjugate lines on the director surface have their parameters of distribution equal in magnitude but opposite in sign.*

5. We shall now consider the normal congruences of Ribaucour in which the surface of reference is an orthogonal surface.

Here $$\gamma \equiv \Sigma X \frac{\partial x_1}{\partial u} = 0 \tag{5·1}$$

and $$\gamma' \equiv \Sigma X \frac{\partial x_1}{\partial v} = 0 \tag{5·2}$$

From the equations (1·3)

$$D' \frac{\partial \phi}{\partial u} - D \frac{\partial \phi}{\partial v} = 0 \tag{5·3}$$

$$D'' \frac{\partial \phi}{\partial u} - D' \frac{\partial \phi}{\partial v} = 0 \tag{5·4}$$

From the two equations (5·3) and (5·4)

either $$DD'' - D'^2 = 0 \tag{5·5}$$

or $$\phi = \text{constant}. \tag{5·6}$$

If $$DD'' - D'^2 = 0$$

then $$\gamma \equiv \Sigma X \frac{\partial x_1}{\partial u} = \frac{D' \frac{\partial \phi}{\partial u} - D \frac{\partial \phi}{\partial v}}{KH}$$

and $$\gamma' \equiv \Sigma X \frac{\partial x_1}{\partial v} = \frac{D'' \frac{\partial \phi}{\partial u} - D' \frac{\partial \phi}{\partial v}}{KH}$$

become indeterminate.

Hence ϕ = constant = C (say).

The necessary and sufficient condition that the congruences of Ribaucour should have the surface of reference as an orthogonal surface is that the Bianchi's characteristic function should be constant.

6. Suppose the surface S is referred to its lines of curvature, then

$$F = 0, \; D' = 0 \tag{6·1}$$

With the help of equation (6·1), equations (1·6), (1·7), (1·8) and (1·9) become

$$e = \frac{D\mathcal{F}\phi}{\mathcal{H}} \; ; f = -\frac{D''\phi\mathcal{E}}{\mathcal{H}} \; ; f' = \frac{D\phi\mathcal{G}}{\mathcal{H}} \; ; g = -\frac{D''\phi\mathcal{F}}{\mathcal{H}} \tag{6·2}$$

But since

$$\mathcal{F} = \frac{1}{H^2}(GDD' - FDD'' - FD'^2 + FD'D''), \tag{6·3}$$

using equations (6·1) in the equation (6·3) we get

$$\mathcal{F} = 0 \tag{6·4}$$

Hence using the equation (6·4) in the equation (6·2)

$$e = g = 0 \tag{6·5}$$

Since in a congruence of Ribaucour the surface of reference is the middle surface, the equation (1·20) for the surfaces of distribution becomes

$$dv \cdot du = 0 \tag{6·6}$$

Using the equations (6·1) and (3·2) we see that the condition of a normal congruence of Ribaucour in which the lines of curvature at the corresponding points of the director surface are parametric is

$$\mathcal{E}\mathrm{D}'' + \mathcal{G}\mathrm{D} = 0 \tag{6·7}$$

From the equations (1·10), (1·11) and (1·12) we get

$$\delta = \mathrm{D}\phi;\ \delta' = \mathrm{D}'\phi;\ \delta'' = \mathrm{D}''\phi. \tag{6·8}$$

Also[9]

$$-y\mathcal{H} = \delta_2 - \delta_1' - \Gamma'\delta + (\Gamma - \Delta')\,\delta' + \Delta\delta'' \tag{6·9}$$

$$y\mathcal{H} = \delta_1'' - \delta_2' + \Gamma''\delta + (\Delta'' - \Gamma')\,\delta' - \Delta'\delta'' \tag{6·10}$$

where $y \left(\equiv \Sigma \mathrm{X} \frac{\partial x_1}{\partial u}\right)$ and $y' \left(\equiv \Sigma \mathrm{X} \frac{\partial x_1}{\partial v}\right)$ are given by the equations (1·3), the subscripts 1, and 2 in δ, δ', δ'' denoting differentiations with regard to 'u' and 'v' respectively. The letters Γ, Γ', Γ''; Δ, Δ', Δ'' have their usual meanings.[10]

With the help of equations (1·3) and (6·1) and (6·8) equations (6·9) and (6·10) become;

$$\mathrm{D}\frac{\partial\phi}{\partial v} = \frac{\partial}{\partial v}(\mathrm{D}\phi) - \Gamma'\mathrm{D}\phi + \Delta\,\mathrm{D}''\phi \tag{6·11}$$

$$\mathrm{D}''\frac{\partial\phi}{\partial u} = \frac{\partial}{\partial u}(\mathrm{D}''\phi) + \Gamma''\mathrm{D}\phi - \Delta'\mathrm{D}''\phi \tag{6·12}$$

But

$$\Gamma' \equiv \frac{\mathcal{G}\mathcal{E}_2 - \mathcal{F}\mathcal{G}_1}{2\mathcal{H}^2} = \frac{\mathcal{E}_2}{2\mathcal{E}};\quad \Delta \equiv \frac{-\mathcal{F}\mathcal{E}_1 - \mathcal{E}\mathcal{E}_2 + 2\mathcal{E}\mathcal{F}_1}{2\mathcal{H}^2} = -\frac{\mathcal{E}_2}{2\mathcal{G}}$$

$$\Gamma'' \equiv \frac{-\mathcal{F}\mathcal{G}_2 - \mathcal{G}\mathcal{G}_1 + 2\mathcal{G}\mathcal{F}_2}{2\mathcal{H}^2} = -\frac{\mathcal{G}_1}{2\mathcal{E}};\quad \Delta' \equiv \frac{\mathcal{E}\mathcal{G}_1 - \mathcal{F}\mathcal{E}_2}{2\mathcal{H}^2} = \frac{\mathcal{G}_1}{2\mathcal{G}}$$

Equations (6·11) and (6·12) reduce to

$$\frac{\partial}{\partial v}\mathrm{D} - \frac{\mathcal{E}_2}{2}\left(\frac{\mathrm{D}}{\mathcal{E}} + \frac{\mathrm{D}''}{\mathcal{G}}\right) = 0$$

$$\frac{\partial}{\partial u}\mathrm{D}'' - \frac{\mathcal{G}_1}{2}\left(\frac{\mathrm{D}}{\mathcal{E}} + \frac{\mathrm{D}''}{\mathcal{G}}\right) = 0$$

Hence D is a function of 'u' only and D″ is a function of 'v' only

$$\therefore\ \frac{\mathrm{D}}{\mathrm{D}''} = \frac{\text{a function of '}u\text{' only}}{\text{a function of '}v\text{' only}}$$

$$\therefore\ \frac{\partial^2}{\partial u\,\partial v}\log\frac{\mathrm{D}}{\mathrm{D}''} = 0 \tag{6·13}$$

and $$D' = 0. \tag{6·14}$$

which shows that in a normal congruence of Ribaucour the lines of curvature of the director surface are isothermal conjugate.

From the equations (6·4), (6·7) and (6·13) we see that

$$\frac{\partial^2}{\partial u \partial v} \log \frac{\mathcal{E}}{\mathcal{G}} = 0$$

and $$\mathcal{F} = 0$$

∴ in a normal congruence of Ribaucour the spherical representations of the surfaces of distribution are isometric.

This can be proved alternately as follows:—

From the equation (3·2) we see that the surface S is minimal.

But the spherical representations of the lines of curvature on a minimal surface are isometric and isothermal conjugate. Therefore the spherical representations of the lines of curvature on the director surface are isometric and isothermal conjugate.

Since the spherical representations of the lines of curvature of the director surface correspond to the spherical representations of the surfaces of distribution, the spherical representations of the surfaces of distribution through a line of a normal congruence of Ribaucour are both isometric and isothermal conjugate.

To summarise:—

The spherical representations of the lines of curvature on the director surface of a normal congruence of Ribaucour are isometric and isothermal conjugate.

The spherical representations of the surfaces of distribution through a line of a normal congruence of Ribaucour are also isometric and isothermal conjugate.

We know that the spherical representations of asymptotic lines on a minimal surface are isometric.

Hence the spherical representations of asymptotic lines on the director surface of a normal congruence of Ribaucour are isometric.

As the spherical representations of asymptotic lines on the director surface correspond to the spherical representations of developable surfaces through a line of a congruence of Ribaucour we get the result:

The spherical representations of developable surfaces through a line of a normal congruence of Ribaucour are also isometric.

7. *Isotropic congruences of Ribaucour.*—We shall find the condition that the congruences of Ribaucour be isotropic.

Since in a congruence of Ribaucour the surface of reference is a middle surface, we must have[11]

$$e = f + f' = g = 0 \tag{7·1}$$

using the equations (7·1) in the equations (1·6), (1·7), (1·8) and (1·9) we have

$$\frac{D}{\mathcal{E}} = \frac{D'}{\mathcal{F}} = \frac{D''}{\mathcal{G}} = \frac{1}{\lambda}\,\text{(say)} \tag{7·2}$$

where

$$\mathcal{E} = D\lambda,\ \mathcal{F} = D'\lambda,\ \mathcal{G} = D''\lambda \tag{7·3}$$

From the equations (1·16), (1·17) and (1·18) we have

$$\frac{D}{E} = \frac{D\mathcal{H}^2}{\mathcal{G}D^2 - 2\mathcal{F}DD' + \mathcal{E}D'^2} = \lambda$$

$$\frac{D'}{F} = \frac{D'\mathcal{H}^2}{\mathcal{G}DD' - \mathcal{F}DD'' - \mathcal{F}D'^2 + \mathcal{E}D'D''} = \lambda$$

$$\frac{D''}{\mathcal{G}} = \frac{D''\mathcal{H}^2}{\mathcal{G}D'^2 - 2\mathcal{F}D'D'' + \mathcal{E}D''^2} = \lambda \text{ using the equation (7·3)}$$

$$i.e., \frac{D}{E} = \frac{D'}{F} = \frac{D''}{G} = \lambda$$

hence the corresponding points are umbilical.[12]

Therefore the necessary and sufficient condition that the congruence of Ribaucour be isotropic is that the corresponding points on the director surface are umbilical, i.e., *that the director surface is a sphere since a sphere is the only real surface all of whose points are umbilics.*

8. We shall now consider the case in which the characteristic function ϕ vanishes.

Putting $\phi = 0$ in the equations (1·4) and (1·5)

$$\frac{\partial x_1}{\partial u} = \frac{\partial y_1}{\partial u} = \frac{\partial z_1}{\partial u} = 0 \tag{8·1}$$

and

$$\frac{\partial x_1}{\partial v} = \frac{\partial y_1}{\partial v} = \frac{\partial z_1}{\partial v} = 0 \tag{8·2}$$

i.e., the surface of reference reduces to a point.

Hence the congruence of Ribaucour in which the characteristic function is zero is a system of rays through a point.

From the equations (8·1) and (8·2) we see that

$$e = f = f' = g = 0$$

Hence if in the congruence of Ribaucour the characteristic function vanishes, then it is a normal isotropic congruence which is a sort of a converse to the known result that the only normal isotropic congruence is a system of rays through a point.

9. *Pseudospherical congruences of Ribaucour.*—We shall now find the condition that the congruence of Ribaucour be pseudospherical.

We know that in a Pseudospherical congruence the mean parameter is constant[13]

i.e., $$\frac{\mathcal{E}\delta'' + \mathcal{G}\delta - 2\mathcal{F}\delta'}{2\mathcal{H}^2} = \text{constant}$$

or $\frac{\mathcal{E}D'' + \mathcal{G}D - 2\mathcal{F}D'}{2\mathcal{H}^2}\phi = \text{constant}$ from (1·10), (1·11) and (1·12)

or $\rho_1 + \rho_2 = \frac{\text{constant}}{\phi}$ where ρ_1 and ρ_2 are the principal radii of curvature at the corresponding point of the director surface.

Hence if the congruence of Ribaucour is Pseudospherical then the sum of the principal radii of curvature at the corresponding point of the director surface varies inversely as Bianchi's characteristic function.

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RANEY NICKEL REDUCTIONS—PART I

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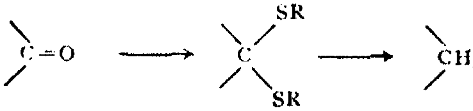
Since Covert and Adkins[1] prepared Raney nickel in a highly active form by treatment of a nickel-aluminium alloy with aqueous sodium hydroxide followed by washing, it has been used for effecting a variety of reactions.[2] Bougault, *et al.*[3] have shown that Raney nickel prepared in the usual manner retains hydrogen and is capable of quantitatively converting thioglycollanilide ($HSCH_2CONH\ C_6H_5$) into acetanilide, and thioglycollic and dithioglycollic acids into acetic acid, without addition of hydrogen. These observations have been considerably extended by Mozingo,[4] who has shown that Raney nickel catalyst removes sulphur from a variety of organic compounds without gaseous hydrogen at moderate temperatures and in the presence of solvents such as alcohol, as follows:

$$RSR' \xrightarrow{Ni(H)} RH + R'H$$

Sulphoxides and sulphones are also similarly reduced. An interesting application of the reduction of carbonyl compounds by Raney nickel to the corresponding methylene derivatives has been mentioned.[5] The carbonyl compound is first converted to the mercaptal which is then subjected to treatment with Raney nickel.

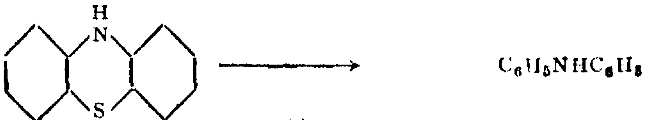


Mozingo[6] has extended the application of Raney nickel to the reduction of compounds other than sulphides, such as ethylenic compounds, aldehydes and ketones. Raney alloy has been directly used in the presence of alkali by Papa[7] for the reduction of several types of compounds. Thus, phenyl ketones, PhCOR, are reduced to the corresponding hydrocarbon $PhCH_2R$, while ketones of the type $Ph\,(CH_2)_x\,COR$, where x is one or more, are reduced to the corresponding carbinol. Various groups attached to the aromatic nucleus are displaced under the conditions used by Papa. For example, halogen is displaced, bromobenzene giving benzene, and *m*-chlorobenzoic acid benzoic acid, in quantitative yields. Simultaneous replacement of halogen by hydrogen and reduction of carbonyl to methylene was also observed. Sulphonic groups are displaced, *o*- and *m*-sulphobenzoic acids being desulphonated in 40 and 50 per cent. yields to benzoic acid. Alkoxyl groups in disubstituted benzene derivatives are replaced by hydrogen when they are situated in the *o*- and *p*-positions with respect to a *m*-directing group. For example, quantitative replacement of the methoxyl group occurs with *o*- and *p*-methoxybenzoic acids, but the *m*-isomer is recovered unchanged.

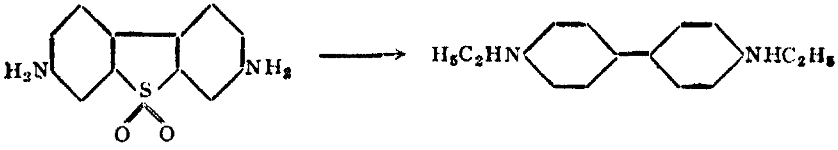
Desulphurisation of heterocyclic compounds containing sulphur by means of Raney nickel under mild conditions without the use of hydrogen does not appear to have been widely studied. Among the very few examples of such reductions may be cited the conversion of biotin methyl ester into dethiobiotin methyl ester.[8] While removal of sulphur occurs when excess of Raney nickel is used, it is possible to effect reductions without removing sulphur using smaller quantities of the reagent. Thus nitrodiphenyl sulphides have been reduced to the corresponding amines by using catalytic quantities of Raney nickel.[9] Dibenzyl sulphide was found to be unaffected when treated with Raney nickel in a Parr hydrogenator at room temperature.

During the course of an investigation of the constitution of the sulphurised vat dyes, Cibanone Yellow R, Cibanone Orange R and Hydron Blue, reduction by Raney nickel was employed for effecting desulphurisation under mild conditions to give sulphur-free degradation products which could then be compared with synthetic products of definite constitution. The valuable data concerning the constitution of these dyes obtained by treatment with Raney nickel will be reported separately.[10] In this paper, the action of Raney nickel on sulphur containing heterocyclic compounds such as thiodiphenylamine (I) and benzidine-sulphone (II), sulphonic acids such as J-acid, and a few other compounds are described.

Thiodiphenylamine (I) in alcohol on treatment with Raney nickel gave diphenylamine; and benzidine-sulphone (II) on similar reduction gave N : N′-diethylbenzidine. N-alkylation during reduction by Raney nickel has also been observed by Mozingo.[6]



(I)



(II)

When J-acid was reduced in aqueous alkaline solution by Raney alloy according to Papa,[7] it gave 6-amino-1-naphthol.

Reduction of β-naphthol in alcoholic alkaline solution gave a mixture of 5 : 6 : 7 : 8-tetrahydro-2-naphthol and 1 : 2 : 3 : 4-tetrahydro-2-naphthol, the latter in a little larger yield. Adkins and Krsek[11] carried out high pressure hydrogenation of β-naphthol in alcohol by means of nickel catalysts prepared by various methods, and obtained both the phenol and alcohol derivatives in proportions depending on the type of catalyst used.

The action of Raney nickel on 2-hydroxy-3-naphthanilide (Brenthol AS); led to 5 : 6 : 7 : 8-tetrahydro-2-hydroxy-3-naphthanilide, identical with the product described by Schröter and Bayer,[12] who prepared it from 5 : 6 : 7 : 8-tetrahydro-2-hydroxy-3-naphthoic acid. The latter compound was obtained by these authors by pressure hydrogenation of 2-hydroxy-3-naphthoic acid, and by Schroeter[13] from 6-hydroxytetralin by means of the Kolbe reaction. Arnold *et al.*[14] also obtained the same acid by the catalytic hydrogenation of ethyl 3-hydroxy-2-naphthoate at 140–150° and under a pressure of 900 lbs., followed by hydrolysis of the ester.

Carbazole has been reported to be resistant to catalytic hydrogenation.[15] Adkins and Coonradt[16] have, however, prepared tetra-, hexa- and dodecahydrocarbazoles in 72, 16 and 85% yields respectively by high pressure reduction of carbazole using Raney nickel or copper chromite catalysts. It has been found in the present work that when carbazole was treated with Raney nickel in boiling morpholine it remained unaffected while reduction in alcohol gave tetrahydrocarbazole (yield, 46%) along with other reduced derivatives. 3-Chlorocarbazole on reduction in alcohol gave a mixture of products from which tetrahydrocarbazole was isolated through the picrate. 3-Aminocarbazole on similar treatment yielded a small quantity of a compound insoluble in dilute hydrochloric acid which was identified as tetrahydrocarbazole, and a very small quantity of an acid-soluble portion which could not be identified.

The behaviour of anthraquinone and 2-methylanthraquinone on treatment with Raney nickel in boiling (1) alcohol, (2) morpholine and (3) aqueous alkali, was studied as a preliminary part of the investigation of the constitution of Cibanone Yellow R and Cibanone Orange R, which are derived from 2-methyl or 2-chloromethylanthraquinone by thionation. Reduction of anthraquinone in the presence of alcohol gave a mixture of products from which octahydroanthraquinone, m.p. 185–86°, was isolated after repeated crystallisations. Reduction in morpholine gave a mixture of different substances from which a colourless crystalline compound, m.p. 226–232°, and a compound crystallising in pale yellow needles, m.p. 182–83°, were isolated by chromatographic separation. The identity of these products has not yet been established. Treatment of anthraquinone with Raney nickel in boiling aqueous alkali gave a colourless crystalline compound, m.p. 267°, as one of the components of the reaction mixture, which analysed for 9: 10-dihydroxyperhydroanthracene ($C_{14}H_{24}O_2$). When 2-methylanthraquinone was reduced in alcohol, a new sterioisomeric form of 2-methyloctahydroanthraquinone, m.p. 137°, was obtained. Reduction of 2-methylanthraquinone in boiling aqueous alkali gave a small quantity of a colourless compound crystallising in needles, m.p. 240–45°, and a mixture of compounds which were liquid at room temperature. A complete analysis of these products will be reported later.

Thioindigo on treatment with Raney nickel in morpholine has given interesting degradation products which are under investigation.

EXPERIMENTAL

Desulphurisation of thiodiphenylamine (*I*).—Thiodiphenylamine (1 g.), Raney nickel, prepared according to Mozingo's method, (10 g.) and alcohol (75 c.c.) were heated under reflux for 4 hours and the mixture was filtered. The Raney nickel residue was washed twice with hot alcohol. The alcoholic extracts were concentrated and cooled and the product (0·55 g.) which separated crystallised from aqueous alcohol in leaflets, m.p. 54°, alone or mixed with an authentic specimen of diphenylamine.

Desulphurisation of benzidine-sulphone (*II*).—Benzidine sulphone (1 g.) was treated with Raney nickel as above. The reduction product (0·55 g.; yield, 70%) crystallised from hot alcohol in needles, m.p. 115° C., and was identical with N: N′-diethylbenzidine. Bamberger and Tichivinsky[17] give m.p. 115–6°. Found: N, 11·8. $C_{16}H_{20}N_2$ requires N, 11·7%).

Desulphurisation of J-acid.—J-acid (10 g.) was dissolved in 10% aqueous sodium hydroxide (450 c.c.), the solution was heated to 90° and Raney alloy (60 g.) was added slowly under stirring (*cf.* Papa, *et. al.*[7]). After the addition of the catalyst, the mixture was further heated for 2 hours. The reaction mixture was filtered and sulphur dioxide was bubbled through the filtrate. 6-Amino-1-naphthol, which separated together with alumina, was extracted with ether. Acetic anhydride (2·5 c.c.) and acetic acid (5 c.c.) were added to the ether-extract and after removal of ether, the solution was heated under reflux for ten minutes and then poured over crushed ice. The diacetyl derivative of 6-amino-1-naphthol separated as a yellow solid which was filtered, washed with cold water and was boiled for 1 minute with ammonia for the removal of the *o*-acetyl group.[18] It was again acidified with acetic acid and the solid (0·2 g.) thus obtained was washed and crystallised from water, when N-acetyl-6-amino-1-naphthol separated as needles, m.p., 98–99°. Sander[18] quotes m.p. 100°. (Found: N, 7·1. $C_{13}H_{11}O_2N$ requires N, 7·0%).

Reduction of β-naphthol.—β-Naphthol (2 g.), Raney nickel (20 g.), alcohol (100 c.c.) and sodium hydroxide (1 g.) were boiled under reflux for 8 hours. After removal of nickel, the solution was acidified and warmed to remove alcohol and then extracted with ether. The ether layer was washed with water and then shaken thrice with 5% sodium hydroxide solution. The alkaline extracts were collected together, acidified and then extracted with ether. After removal of ether, the alkali-soluble reduction product was left behind as an oil (0·54 g.). On shaking the oil with benzoyl chloride in aqueous sodium hydroxide, the benzoyl derivative of 5 : 6 : 7 : 8-tetrahydro-2-naphthol was obtained which on crystallisation from aqueous alcohol gave m.p. 95–96°. Heilbron[19] gives m.p. 96°. The ether extracts containing the alkali insoluble 1 : 2 : 3 : 4-tetrahydro-2-naphthol gave a brown oil (0·7 g.) after removal of the solvent. When heated with phenyl isocyanate it gave the corresponding phenylurathane which crystallised from light petroleum (60–80°) and benzene as needles, m.p. 98–99°. Bamberger and Lodter[20] give m.p. 99°.

Reduction of Brenthol AS

Brenthol AS (2 g.), Raney nickel (20 g.), methyl alcohol (40 c.c.) and sodium hydroxide (1 g.) were heated under reflux for 5 hours. The mixture was filtered while hot and the nickel residue was washed twice with methyl alcohol. On cooling, the unreacted Brenthol AS separated. The more soluble portion after crystallisation from methyl alcohol gave 5 : 6 : 7 : 8 tetrahydro-2-hydroxy-3-naphthanilide as colourless needles, m.p. 185–87°, unaltered by further recrystallisation from the same solvent. Schröter and Bayer[12] quote m.p. 183°. (Found: C, 76·4; H, 6·1; N, 5·5. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%.)

Reduction of Carbazole

Method A.—Carbazole (2 g.), Raney nickel (20 g.) and morpholine (50 c.c.) were heated under reflux for 8 hours and filtered and the residue was extracted with hot morpholine. The filtrate and the washings were collected and poured over a mixture of ice and hydrochloric acid. The solid obtained on crystallisation was found to be unreacted carbazole.

Method B.—Carbazole (4 g.), Raney nickel (80 g.) and ethyl alcohol (250 c.c.) were heated under reflux for 6 hours. After the separation of nickel, the alcohol in the reaction mixture was removed by distillation. The reduction product was isolated by means of ether and when purified according to Adkins and Coonradt,[16] gave 0·3 g. of unreacted carbazole, 1·9 g. (yield, 46%) of tetrahydrocarbazole, m.p. 110° and 0·2 g. of a mixture of octa and dodecahydrocarbazole. The tetrahydrocarbazole after crystallisation from aqueous alcohol gave lustrous flakes, m.p. 112°, alone or mixed with authentic tetrahydrocarbazole. It was further characterised by the preparation of its picrate which crystallised from alcohol in red brown needles, m.p. 142–43°. Adkins and Coonradt[16] give m.p. 145–145·5°.

Reduction of 3-*chlorocarbazole*

3-Chlorocarbazole (1 g.), Raney nickel (10 g.) and alcohol (50 c.c.) were refluxed for 5 hours and then filtered. The filtrate on concentration and cooling, gave a white solid (0·65 g.), m.p. 125–35°, which did not contain chlorine. It was recrystallised from aqueous alcohol but the m.p. was unaltered. The substance was, therefore, treated with picric acid and the picrate obtained was crystallised from alcohol, m.p. 145°, unaltered when recrystallised from the same solvent. Adkins and Coonradt[16] give the m.p. of tetrahydrocarbazole picrate as 145–145·5°. The picrate on decomposition with 1% ammonia, gave tetrahydrocarbazole as a white solid which crystallised from aqueous alcohol in lustrous white flat needles, m.p. 119–20°. Perkin and Plant[21] give m.p. 116°.

Reduction of 3-*aminocarbazole*

3-Aminocarbazole (2 g.), Raney nickel (20 g.) and dioxan (60 c.c.) were heated under reflux for 8 hours. After removal of nickel, the solvent was removed by distillation and the residue was extracted with ether. The ether extract was shaken repeatedly with 15% hydrochloric acid. It was then washed, dried and ether was removed. The pinkish white solid (0·14 g.) obtained gave a picrate, m.p. 142°, alone or mixed with authentic tetrahydrocarbazole-picrate. The small quantity of acid-soluble portion obtained could not be identified.

Reduction of Anthraquinone

Method A.—Anthraquinone (1·5 g.), Raney nickel (10 g.) and alcohol (60 c.c.) were boiled under reflux for 3 hours and then filtered while hot. The alcoholic solution after concentration and cooling gave yellow needles, m.p. 168–72° (0·67 g.), raised to 185–6° after three recrystallisations from alcohol. Skita[22] gives the m.p. of octahydroanthraquinone as 185–6°, (Found: C, 77·2; H, 7·3. $C_{14}H_{16}O_2$ requires C, 77·8; 7·4%.) After prolonged standing (six months), the analytical specimen turned orange and softened above 150° and melted at 170–74°.

Method B.—Anthraquinone (2 g.), Raney nickel (20 g.) and morpholine (60 c.c.) were heated under reflux for 12 hours and then filtered hot. The filtrate was poured over ice and concentrated hydrochloric acid, and the solid (0·96 g.) which separated was filtered, washed and dried. The substance dissolves in alkaline sodium hydroxide solution giving a colourless solution from which it could be recovered by air oxidation. The reduction product was dissolved in chloroform and passed through an activated alumina solution and the pale green major fraction after concentration gave a crystalline solid, m.p. 226–32°. The chloroform mother-liquor after concentration and addition of alcohol gave pale yellow flat needles, m.p. 182–3° unaltered by further crystallisation from the same solvent (Found: C, 75·9; H, 7·1%).

Method C.—Anthraquinone (2 g.), Raney nickel (20 g.), sodium hydroxide (2 g.) and water (100 c.c.) were heated under reflux for 8 hours. The mixture was acidified with hydrochloric acid and then filtered and the residue was washed and dried. It was extracted with chloroform (200 c.c.) and the chloroform solution after concentration and cooling gave colourless flat elongated plates, m.p. 257–62°, raised to 267–8° after recrystallisation from alcohol. (Found: C, 75·5; H, 11·0. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·7%.) The substance is insoluble in hot aqueous sodium hydroxide and alkaline hydrosulphite. The mother-liquor, after the separation of the above crystalline product, gave a sticky solid (O·85 g.) after removal of the solvent.

Reduction of 2-methylanthraquinone

Method A.—2-Methylanthraquinone (2 g.) when reduced as in Method A for anthraquinone, gave a yellow reduction product (0·8 g.), m.p. 95–99°, which after two crystallisations from alcohol gave m.p. 137°. Elementary analysis of the product is in agreement with methyl octa hydroanthraquinone. Skita[22] quotes m.p. of 2-methyl-1:2:3:4:5:6:7:8-octahydroanthraquinone as 158–9°· (Found: C, 78·0; H, 7·5. $C_{15}H_{18}O_2$ requires C, 78·3; H, 7·8%.) The reduction product on standing turns orange as in the case of the reduction product from anthraquinone.

Method B.—2-Methylanthraquinone (2 g.) was treated as in Method B for anthraquinone. The sticky product (0·9 g.) obtained after three recrystallisations from alcohol, gave a substance melting constantly at 170–72°, undepressed when mixed with 2-methylanthraquinone, *Method C.*—2-Methylanthraquinone (4 g.) was treated as in Method C for anthraquinone. The nickel residue was extracted with benzene and the benzene extract after concentration and cooling gave a colourless crystalline solid. It softened above 235° and melted at 242–6°. The melting point was unaltered by further recrystallisation from benzene and light petroleum. The mother-liquor after the separation of the above crystalline product gave a viscous orange yellow liquid (2·1 g.) on removal of the solvent. It was redissolved in benzene and chromatographed through alumina. Several fractions separated on eluting the chromatogram with benzene but led only to oily products which could not be further purified.

SUMMARY

Treatment of sulphur-containing heterocyclic compounds such as thiodiphenylamine (I) and benzidine-sulphone (II) with Raney nickel in a suitable solvent gave the sulphur-free compounds diphenylamine and N: N′-diethylbenzidine (reduction in ethyl alcohol).

β-Naphthol gave a mixture of 1:2:3:4-tetrahydro-2-naphthol and 5:6:7:8-tetrahydro-2-naphthol on reduction with Raney nickel in alcoholic alkaline solution. Naphthol AS (2-hydroxy-3-naphthanilide) yielded 5:6:7:8-tetrahydro-2-hydroxy-3-naphthanilide and J-acid gave 6-amino-1-naphthol on treatment with Raney nickel.

Carbazole was unaffected when treated with Raney nickel in morpholine, but gave tetrahydrocarbazole when reduced in alcohol. 3-Chloro- and 3-aminocarbazole also gave tetrahydrocarbazole on reduction in alcohol and dioxan respectively.

Anthraquinone and 2-methylanthraquinone gave octahydro-derivatives on reduction in alcohol. Reduction in morpholine and in aqueous alkali gave several reduction products which are under investigation.

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A NEW SYNTHESIS OF 4-HYDROXYCOUMARINS

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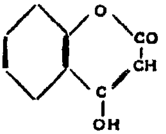
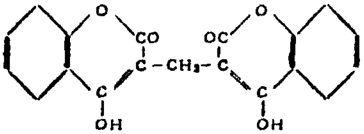
Roderick[1] and Schofield[2] noticed a hemorrhagic disease in cattle and showed that it was due to badly cured hay made from sweet clover. Campbell and Link[3] isolated this anticoagulant factor from spoiled sweet clover hay, and determined its structure to be 3: 3′-methylene-bis-4-hydroxycoumarin (II) by alkaline degradation and cleavage with phenylhydrazine. The constitution has been confirmed by its synthesis from 4-hydroxycoumarin (I) and formaldehyde.[4] In view of the anticoagulant properties of 3-substituted-4-hydroxycoumarins,[5] methods for the synthesis of 4-hydroxycoumarins (I) have assumed importance.



(I)

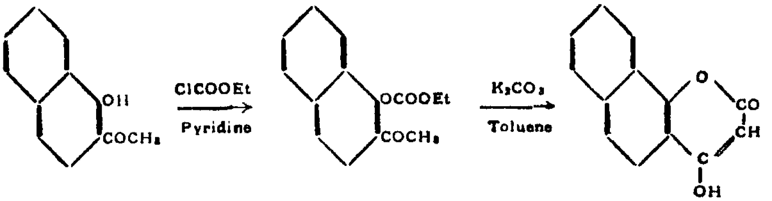


(II)

Three general methods for the synthesis of 4-hydroxy-coumarins have so far been described: (1) *O*-Acetoxybenzoyl chlorides are condensed with malonic ester, cyanacetic ester or acetoacetic ester in presence of sodium, when the corresponding 3-substituted-4-hydroxycoumarins are formed, which are then hydrolysed to 4-hydroxycoumarins.[6] (2) Cyanacetic ester is condensed with phenols[7] according to the method of Hoesch, which is limited to the use of *m*-dihydric phenols. In some cases, the hydrolysis of the intermediate ketimine hydrochloride is difficult. (3) The cyclisation of the *O*-acetyl derivative of an ester of salicylic acid by means of sodium at high temperature[8] gives low yields of 4-hydroxycoumarins.

Earlier work carried out by one of us and others on the transformation of *o*-benzoyloxyacetophenones to dibenzoylmethanes by means of sodamide,[9] potassium carbonate[10] or sodium in toluene,[11] indicate that an application of this reaction to the *O*-carbethoxy-derivatives of *o*-hydroxyacetophenones might lead to a new general method for the synthesis of 4-hydroxycoumarins. We have now examined the scope of this reaction by model experiments on the behaviour of the *O*-carbethoxy derivative (IV) of the readily available

2-acetyl-1-naphthol (III) towards sodamide,[9] anhydrous potassium carbonate,[10] metallic sodium and sodium ethoxide[11] in appropriate solvents.



(III) (IV) (V)

When the ester (IV) was treated with potassium carbonate in toluene, 4-hydroxynaphthocoumarin (V) was obtained in an optimum yield of 45 per cent., but the reaction did not proceed solely in the desired direction.

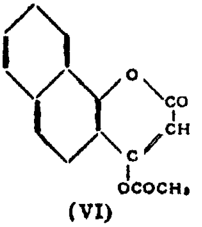
The preparation of the ester (IV), which proved difficult initially due to its instability resulting in hydrolysis to (III), had to be carried out under closely defined conditions. When ethyl chlorocarbonate was added to (III) in pyridine solution in the cold, an instantaneous reaction took place, and by working up the product immediately a quantitative yield of (IV) was obtained. Treatment of (IV) with potassium carbonate in toluene gave a mixture of products (A) and (B), which could be easily separated either by taking advantage of the insolubility of (A) and of the ready solubility of (B) in chloroform, or by extracting with sodium bicarbonate solution in which (A) alone was soluble. The product (A) when obtained in this manner was almost pure, while (B) could only be purified by chromatographic adsorption or by crystallisation from acetic acid. Comparatively lower yields of the products (A) and (B) were obtained when the transformation was carried out with metallic sodium in toluene.

The product (A) crystallised from alcohol or dioxane in small, colourless needles, m.p. 279–80° (decomp.). 4-Hydroxy-naphthocoumarin (V) has been prepared by Anschutz[12] by the condensation of 1-hydroxy-2-naphthoyl chloride with sodio-malonic ester, followed by hydrolysis of the 3-carbethoxy-4-hydroxynaphthocoumarin. He has described this as greyish white crystals, m.p. 256–8°. On repeating Anschutz's work we obtained the intermediate 3-carbethoxy-derivative as yellow needles, m.p. 179° (Anschutz, m.p. 179°). This on hydrolysis gave 4-hydroxynaphthocoumarin as colourless needles, m.p. 279-80°, identical with (A) in all respects. A similar discrepancy in the melting point has been noticed in the case of 3:3′-methylene-bis-4-hydroxycoumarin (II), which was first synthesised by Anschutz, who gave the m.p. 260°, and later by Stahmann, *et al.*[4] who gave the m.p. 288–89°; natural dicoumarin has m.p. 288–89°.

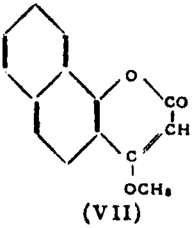
When the intramolecular condensation of the ester (IV) was carried out with sodamide in ether, substance (B) and acetonaphthol (III) were the only products isolated. In a few of the experiments while the product after the sodamide reaction was being worked up, it turned violet on exposure to air; and from the mixture a small quantity of (B), (III) and a violet compound (C) could be isolated by chromatography. The exact conditions for this transformation could however not be ascertained. The condensation of the ester with sodium methoxide in ether gave a 5 per cent. yield of product (B), the rest of the ester being hydrolysed to (III). When sodium ethoxide in alcohol was used, the ester merely underwent hydrolysis to (III).

While this work was in progress Boyd and Robertson[13] described a one-step synthesis of 4-hydroxycoumarins in excellent yields from *o*-hydroxyacetophenones by treatment with ethyl carbonate in presence of metallic sodium. By carrying out the same reaction on (III), a nearly quantitative yield of 4-hydroxynaphthocoumarin (V) could be obtained. For the preparation of 4-hydroxycoumarins, Boyd and Robertson's method is therefore superior to our method *via* the carbethoxy derivatives of *o*-hydroxyacetophenones.

4-Hydroxynaphthocoumarin (V) dissolves in sodium bicarbonate solution with effervescence, and on acidification the hydroxycoumarin is precipitated unchanged. It could be titrated with alkalis using phenolphthalein as indicator. After boiling for 2 to 3 hours with 10 per cent. aqueous or alcoholic alkali, 4-hydroxynaphthocoumarin could be recovered unchanged by acidification. On fusion with caustic potash, it gave a quantitative yield of 1-hydroxy-2-naphthoic acid. It remained unaffected by treatment with cold concentrated sulphuric acid. When heated above its melting point, a mixture of products was obtained, from which 1-acetyl-2-naphthol (III) and an unidentified product (D), m.p. 306–7°, were isolated by chromatography. The hydroxycoumarin (V) gave an acetyl derivative (VI) by long boiling with acetic anhydride, and a methyl ether (VII) by treating its solution in acetone with excess of diazomethane in ether. Coupled with diazotised *p*-nitraniline in aqueous alkaline solution or in alcohol in presence of sodium acetate, (V) gave a yellowish orange dye, 3-*p*-nitrobenzeneazo-4-hydroxynaphthocoumarin (VIII). Huebner and Link[14] have shown that

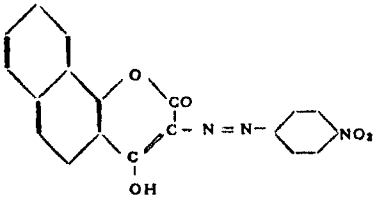


(VI)

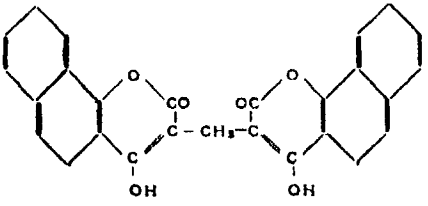


(VII)

4-hydroxycoumarin (I) couples with diazonium salts to give 3-azoderivatives. On treatment of a hot alcoholic solution of (V) with excess of formaldehyde 3:3′-methylene-bis-4-hydroxy-naphthocoumarin (IX) was obtained. 4-Hydroxynaphthocoumarin (V) could not be converted into product (B) by treatment with potassium carbonate in toluene.



(VIII)



(IX)

The product (B) crystallised from acetone or acetic acid as greenish yellow, thin elongated plates, m.p. 244–5°. It was phenolic in character and gave a light olive colouration with ferric chloride. It gave a *p*-nitrobenzoate, and an acetate on treatment with acetic anhydride and a drop of pyridine or with acetic acid in presence of hydrochloric acid. It did not form a dinitrophenylhydrazone under the usual conditions. Its yellowish orange alcoholic alkaline solution turned deep red on standing in the cold, and a deep violet compound was isolated by acidification, identical with the product (C) obtained earlier. Treatment with hot alcoholic alkali completely decomposed (B). Fusion of (B) with potassium hydroxide yielded 1-hydroxy-2-naphthoic acid, and a small quantity of a reddish-violet phenolic compound. A deep red dye was obtained by coupling (B) with diazotised aniline, and a yellow crystalline product (E), m.p. 345–50°, was obtained on treatment of product (B) with cold concentrated sulphuric acid. Attempts to convert (B) into (III) were unsuccessful. The analytical data for (B) and its derivatives correspond with the molecular formula $C_{25}H_{16}O_4$. The constitution of this compound will be discussed in a later communication.

EXPERIMENTAL

O-Carbethoxy-2-acetyl-1-naphthol (IV)

To a cooled solution of 2-acetyl-1-naphthol (10 g.) in pyridine (30 c.c.) ethyl chlorocarbonate (15 c.c.) was added drop by drop with shaking, when an instantaneous reaction took place. The reaction mixture was immediately stirred into crushed ice and hydrochloric acid. The precipitate crystallized from alcohol in thin colourless flakes (11 g.), m.p. 76° (Found: C, 70·1; H, 5·7. $C_{15}H_{14}O_4$ requires C, 69·8; 5·4%).

4-Hydroxynaphthocoumarin (V) and product (B)

(i) The compound (IV) (2 g.), toluene (20 c.c.) and freshly ignited potassium carbonate (6 g.) were refluxed under stirring for 12 hours. The potassium salt was filtered from the deep violet coloured toluene solution which on treatment with norit for a long time gave some unconverted (IV). The greyish green potassium salt was decomposed with dilute acetic acid, filtered and treated thrice with hot chloroform, when a part went into solution. The residue (0·8 g.) which was 4-hydroxynaphthocoumarin (V) crystallised from alcohol or dioxane in small colourless needles, m.p. 279–80° (Found: C, 73·1; H, 4·0; M.W. by titration, 225. $C_{13}H_8O_3$ requires C, 73·5; H, 3·9%; M.W. 212).

The chloroform extract on concentration and chromatography gave product (B), which crystallised from acetic acid in greenish yellow long thin plates (0·2 g.), m.p. 244–45° (Found: C, 78·5; H, 4·3. $C_{25}H_{16}O_4$ requires C, 78·9; H, 4·2%).

The separation of 4-hydroxynaphthocoumarin (V) and product (B) could also be very readily effected by macerating the product, obtained after decomposing the potassium salt, with acetic acid, with sodium bicarbonate solution, when (V) could be obtained from the soluble part by acidification, while (B) was obtained as the residue.

(ii) 3-Carbethoxy-4-hydroxynaphthocoumarin, obtained by treating 1-acetoxy-2-naphthoyl chloride in benzene with sodio-malonic ester in benzene for 8 hours at room temperature and for two hours on the water-bath, crystallised from alcohol in yellow needles, m.p. 179° (Anschutz, m.p. 179°). It gave a red colour with ferric chloride and was soluble in aqueous sodium bicarbonate. 4-Hydroxynaphthocoumarin (V) was obtained by hydrolysis of the 3-carbethoxy derivative by refluxing with excess of 1·5 per cent. potassium hydroxide solution for 12 hours, as colourless needles from alcohol, m.p. 279–80° (Anschutz, greyish white needles, m.p. 256–8°), identical with the product obtained by the action of potassium carbonate on (IV).

(iii) 2-Acetyl-1-naphthol (III) (1·5) g.), ethyl carbonate (40 c.c.) and metallic sodium (2·5 g.) were heated on the water-bath for 30 minutes, excess of sodium destroyed by means of methyl alcohol, the sodium salt dissolved in water, acidified, and the light cream-coloured precipitate filtered, (1·4 g.). It crystallised from alcohol in thin colourless needles, m.p. 279–80°, identical with 4-hydroxynaphthocoumarin (V).

4-Hydroxynaphthocoumarin (V) gives a light orange colour with ferric chloride. It is very sparingly soluble in chloroform, benzene or toluene.

It dissolves in concentrated sulphuric acid with a brownish orange colour, having a light green fluorescence.

Decarboxylation of 4-hydroxynaphthocoumarin:

When (V) (0·2 g.) was heated at 285° for two minutes, it melted with the evolution of carbon dioxide. The brownish red melt was taken up in chloroform, and the chloroform solution chromatographed through alumina, when it separated into two definite bands. The lesser absorbed yellow band on elution with chloroform gave a phenolic product, which crystallised from alcohol in yellow needles, m.p. 98°, and was identified by mixed m.p. to be 2-acetyl-1-naphthol (III). The column of alumina containing the second band on treatment with hot alcohol gave a non-phenolic product, which crystallised from alcohol in small yellow plates, m.p. 306–7° (with darkening in colour) Product (D). It was too little to be worked up further.

Fusion of (V) with potassium hydroxide

Potassium hydroxide (2 g.) and water (0·5 c.c.) were heated in a nickel crucible till a clear solution was obtained, and (V) (0·5 g.) added. The substance began to go into solution at 240° and gave a clear yellow solution at 280°, at which temperature it was maintained for 15 minutes. On cooling, the yellow product was dissolved in water (20 c.c.) and carbon dioxide passed through the solution till it was no longer alkaline to phenolphthalein. A light brown shining crystalline precipitate separated, which was filtered (0·4 g.) and proved to be a potassium salt. It was dissolved in the minimum quantity of alcohol and precipitated with dilute hydrochloric acid. Crystallised from alcohol, it had m.p. 190–91°, and was identified as 1-hydroxy-2-naphthoic acid. The filtrate, after the separation of the potassium salt, on acidification and ether extraction, yielded a small quantity of a phenolic light brown crystalline substance, m.p. 89–93°; the alcoholic solution gave a green colour with ferric chloride.

4-*Acetoxynaphthocoumarin* (*VI*), obtained by refluxing (V) with acetic anhydride for 2 hours, crystallised from benzene in light yellow shining plates, m.p. 134–35° (Found: C, 70·4; H, 3·9; Acetyl 17·1. $C_{16}H_{10}O_4$ requires C, 70·8; H, 3·9; Acetyl 16·9%). It is insoluble in cold sodium bicarbonate solution, but can be readily hydrolysed by warming with alkalis, or even by hot water or alcohol to the parent 4-hydroxynaphthocoumarin.

4-*Methoxynaphthocoumarin* (*VII*), obtained by treating a solution of (V) (0·2 g.) in dry acetone (20 c.c.) with diazomethane in ether, crystallised from alcohol in thin colourless needles, m.p. 218° (Found: C, 74·4; H, 4·6. $C_{14}H_{10}O_3$ requires C, 74·3; O, 4·4%).

3-*p*-*Nitrobenzeneazo-4-hydroxynaphthocoumarin* (*VIII*)

A diazotised solution from *p*-nitraniline (0·3 g.) was added to a solution of (V) (0·2 g.) in sodium hydroxide, and the mixture stirred for one hour, keeping the coupling bath alkaline throughout. The dye, obtained by acidifying the wine-red solution, crystallised from nitrobenzene in yellowish orange needles or from acetic acid in small red shining plates, m.p. 318° (Found: N, 11·5. $C_{19}H_{11}O_5N_3$ requires N, 11·6%). The same dye was also obtained when the coupling was done in alcohol in presence of sodium acetate.

3:3′-*Methylene-bis-4-hydroxynaphthocoumarin* (*IX*)

To a hot solution of (V) (0·15 g.) in alcohol (4 c.c.), formaldehyde (40 per cent.; 1 c.c.) was added, and the mixture heated when a white crystalline precipitate separated immediately. It was filtered while hot and crystallised from trichlorobenzene in fine thin needles (0·14 g.) melting with decomposition above 300° (Found: C, 73·7; H, 4·0. $C_{27}H_{16}O_6$ requires C, 74·3; H, 3·7%). The substance is insoluble in benzene, toluene, dioxane and chloroform.

Transformation of (*IV*) *with sodamide*

The ester (IV) (2 g.), ether (10 c.c.) and powdered sodamide (2 g.) were shaken at room temperature for 8 hours, and allowed to stand overnight. The yellowish orange coloured solid that separated was filtered and stirred into acetic acid, and the dirty green sticky product thus obtained, solidified after keeping in the refrigerator. It was taken up in hot acetone (norit) and cooled, and the crystalline product that separated was recrystallised from acetic acid. The greenish yellow plates (0·4 g.), m.p. 244–5°, were identical with product (B). The acetone filtrate on evaporation gave 2-acetyl-1-naphthol (III).

Product (B) is very sparingly soluble in alcohol. It gives light olive colour with ferric chloride. It is insoluble in cold sodium carbonate solution and sparingly soluble in cold sodium hydroxide solution, but very soluble in alcoholic alkali giving a reddish yellow solution. It dissolves in concentrated sulphuric acid giving a deep red solution, which when poured over chipped ice gave a bright yellow product (E) crystallising from alcohol in yellow needles, m.p. 345–50°. (with decomp.). (Found: C, 57·1; H, 5·4%.) The substance (E) is soluble in warm sodium carbonate solution and cold caustic soda solution and gives an olive green colouration with ferric chloride. Product (B) on fusion with potassium hydroxide as in the case of

(V), gave 1-hydroxy-2-naphthoic acid and a deep violet product which is being examined.

The *acetate* of product (B), obtained by refluxing with acetic anhydride and a drop of pyridine, crystallised from acetic acid in small light yellow plates, m.p. 234–5° (Found: C, 76·2; H, 4·6; Acetyl 11·0. $C_{27}H_{18}O_6$ requires C, 76·5; H 4·3; Acetyl, 10·0%).

The p-*nitrobenzoate* of (B), prepared by treatment with *p*-nitrobenzoyl chloride in pyridine on the water-bath for 30 minutes, crystallised from acetic acid in small light yellowish brown plates, m.p. 258–60°, after shrinking at 255° (Found: N, 2·6. $C_{32}H_{19}O_7N$ requires N, 2·6%).

When product (B) (0·2 g.), dissolved in 2 per cent. alcoholic alkali, was coupled with diazotised aniline, stirred for 2 hours, a deep red solution was obtained, which on acidification gave a deep red dye. It could not be crystallised, but was purified by precipitation from a benzene solution by petroleum ether (60–80°), when it was obtained as an amorphous powder which decomposed above 180° (Found: N, 5·7. $C_{31}H_{20}O_4N_2$ requires N, 5·4%).

Decomposition of product (B) with alcoholic alkali

Product (B) (0·5 g.) was dissolved in 2 per cent. alcoholic caustic soda solution and the yellowish red solution kept overnight at room temperature. Carbon dioxide was passed through the solution, which had become deep red; but only sodium carbonate was precipitated and the colour of the solution became violet. The violet coloured filtrate was acidified, and the deep violet precipitate collected. The filtrate on evaporation gave a sticky violet-coloured product which could not be crystallised. The precipitate on purification by chromatography through alumina using benzene as solvent gave a violet-coloured compound which crystallised from benzene in greyish violet laminary plates (Product C) (0·2 g.), decomposing at 174–6°. The substance is not soluble in aqueous sodium carbonate or sodium hydroxide solution. It dissolves in hot alcoholic alkali to give a brownish red solution, and dissolves in alcohol to give a violet coloured solution, which gives with ferric chloride a cherry red colouration, and with a drop of hydrochloric acid a reddish brown colour. It gives a brownish orange solution in concentrated sulphuric acid, exhibiting a bright green fluorescence.

SUMMARY

4-Hydroxynaphthocoumarin has been synthesised by the internal condensation of *O*-carbethoxy-2-acetyl-1-naphthol, thus suggesting a new general

method for the synthesis of 4-hydroxycoumarins. The behaviour of 4-hydroxynaphthocoumarin has been studied; its derivatives including the corresponding dicoumarin have been prepared. By the action of potassium carbonate or sodamide on the carbethoxy ester of 2-acetyl-1-naphthol, a second product was obtained, the constitution of which is under examination.

We wish to thank Mr. T. S. Gore for carrying out the microanalyses and the Trustees of the Sir Dorabji Tata Trust for a scholarship awarded to one of us.

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6: 7-BENZOCOUMARANONE

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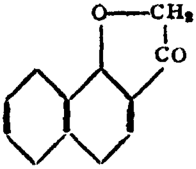
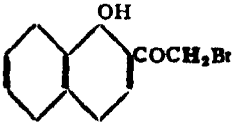
In the course of a study of the action of alkaline condensing agents on ethyl 2-acetyl-1-naphthyl carbonate,[1] it appeared that a possible product was 6: 7-benzocoumaranone (I), and the substance had to be prepared for a direct comparison. It was first described by Ullmann,[2] who prepared it by the cyclization of 2-bromacetyl-1-naphthol (II) and recorded the m.p. 91–92°.

Fries,[4] quoting van Paul Lanz,[3] has stated that a benzocoumaranone constituted as (I) and melting at 116°, is obtained by the intramolecular acylation of α-naphthoxyacetyl chloride (III); the m.p. was slightly higher (119°), when the corresponding bromide was used. Ingham, Stephen and Timpe,[5] who have not referred to the work of Fries and Lanz, carried out the intramolecular acylation of α-naphthoxyacetyl chloride (III) with aluminium chloride in benzene, and obtained a product, m.p. 119°, which they considered to be the *peri*naphthopyrone (IV), rather than the coumaranone (I), since it condensed with benzaldehyde to form the benzylidene derivative, which could not be converted through its dibromide into the corresponding flavonol. Another argument advanced in favour of (IV) was the non-identity of its melting point with that of 6: 7-benzocoumaranone (I), reported



(I)



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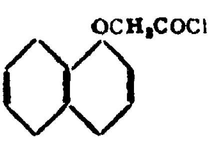

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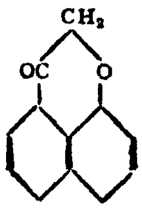
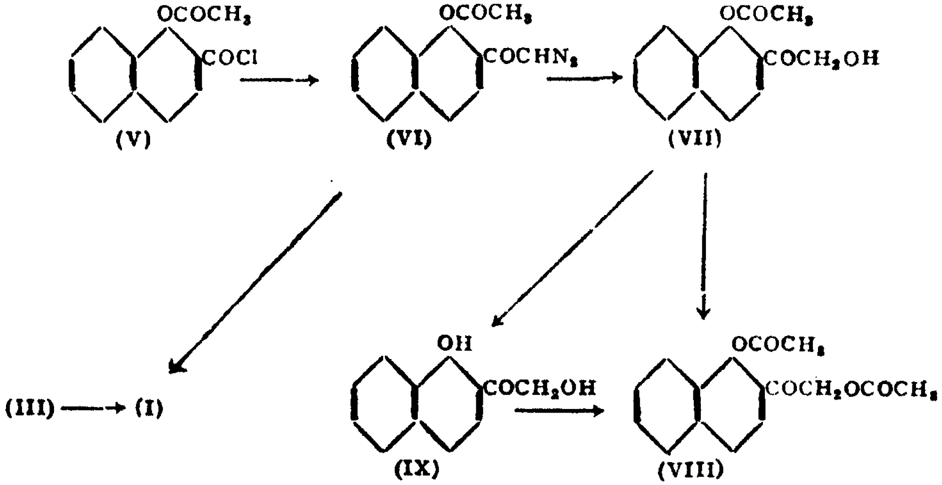


(IV)

to have been synthesised by Ullmann[5] by an unambiguous method from 2-bromacetyl-1-naphthol (II) in which the 1:2-position is already fixed. Several similar instances of *peri*-ring closure are known such as the condensation of α-naphthylacetyl chloride to give acenaphthenone, and the formation of benzanthrone from α-benzoylnaphthalene in presence of aluminium chloride.

Reviewing Ullmann's work[5] on the ω-bromination of 2-acetyl-1-naphthol, it was found that conflicting results have been recorded for this bromination. Ullmann obtained 2-bromacetyl-1-naphthol (II) (m.p. 124·5°) by brominating acetonaphthol or its acetyl derivative in carbon tetrachloride solution, while Torrey and Brewster[6] obtained 4-bromo-2-acetyl-1-naphthol, m.p. 127°, under the same conditions. Fries[7] also failed to get (II), and it has now been found that even bromination with N-bromosuccinimide, which normally leads to ω-bromination, yields 4-bromo-2-acetyl-1-naphthol. Bromination in acetic acid with two molecules of bromine gave a quantitative yield of the ω-4-dibromo derivative.

6:7-Benzocoumaranone (I) has now been synthesised by an unambiguous route starting from 1-hydroxy-2-naphthoic acid, through the intermediate diazoketone, by the following scheme.



The acid chloride (V) of the acetate of 1-hydroxy-2-naphthoic acid, on treatment with an etheral solution of diazomethane gave the diazoketone (VI). This on treatment with dilute sulphuric acid in dioxane gave the carbinol (VII), which on acetylation gave the corresponding acetate (VIII). Eistert[8] has shown that the corresponding diazoketone from 2-hydroxy-3-naphthoic acid gives the benzocoumaranone on treatment with alcohol and dilute sulphuric acid, but the diazoketone (VI) when treated under similar conditions gave the carbinol (VII). Eistert[8] further found that the corresponding carbinol from 2-hydroxy-3-naphthoic acid, on longer treatment with alcohol and sulphuric acid, also gave the benzocoumaranone. It was found, however, that the carbinol (VII) under similar conditions gave merely the deacetylated compound (IX), which was also obtained by treatment of the carbinol (VII) with sodium hydroxide. This gave the same diacetate (VIII) as that obtained from the carbinol (VII). However, the diazoketone (VI) on treatment with concentrated sulphuric acid in the cold gave a compound, m.p. 119°, which from its properties and those of its derivatives proved to be 6:7-benzocoumaranone (I). The carbinol (VII) or (IX) did not give the 6:7-benzocoumaranone under the same conditions. As the 6:7-benzocoumaranone had the same melting point and properties as those described by Ingham[5] *et al.* for their product, obtained by the intramolecular acylation of α-naphthoxyacetyl chloride, it was considered desirable to repeat their work.

The acid chloride, prepared by the action of phosphorus pentachloride on α-naphthoxyacetic acid, gave on treatment with aluminium chloride in benzene a substance, m.p. 119°, identical in all respects with 6:7-benzocoumaranone. Thus cyclization of α-naphthoxyacetyl chloride takes place in the 2-position and not in the *peri* position.

EXPERIMENTAL

1-*Acetoxy-2-naphthyl diazomethyl ketone* (*VI*).—1-Acetoxy-2-naphthoic acid, obtained by refluxing 1-hydroxy-2-naphthoic acid with four parts of 1:1-mixture of acetic acid and acetic anhydride for three hours, crystallised from benzene in colourless needles, m.p. 156°. The acetate was unstable to long keeping, and to the action of hot water or even hot alcohol. The acid chloride, m.p. 114°, was obtained by treatment with thionyl chloride in petroleum ether (60–80).

The finely powdered acid chloride (5 g.), dissolved in ether (100 c.c.), was added dropwise in the course of one hour to an agitated, ice-cold solution of diazomethane in ether, prepared from nitrosomethylurea (12 g.), 40% potassium hydroxide (30 c.c.) and ether (100 c.c.), and kept in the refrigerator for 24 hours. The diazoketone which separated as a light yellow crystalline precipitate was filtered (3 g.) and the filtrate on concentration gave more of the diazoketone. The substance crystallised from benzene in small shining plates (3·2 g.), m.p. 131° (decomp.) (Found: N, 11·2. $C_{14}H_{10}O_3N_2$ requires N, 11·0%.) It decomposes on long standing. It dissolves in concentrated sulphuric acid with decomposition giving a deep orange solution, with a bright green fluorescence.

1-*Acetoxy-2-naphthoylcarbinol* (*VII*).—To a solution of the diazoketone (VI) (0·5g.) in dioxane (10 c.c.), 2N sulphuric acid (2 c.c.) was added with shaking, and the solution allowed to stand at room temperature for two hours. The diazoketone slowly gave off nitrogen, and the solution became slightly deeper in colour. On dilution with water, the crystalline precipitate was collected and crystallised from alcohol. The shining yellow flat plates (0·35 g.) had m.p. 121°. (Found: C, 69·1; H, 4·9. $C_{14}H_{12}O_4$ requires C, 68·8; H, 4·9%.) The substance gives a deep green colour with ferric chloride, and an orange solution in concentrated sulphuric acid, and dissolves in cold 1% caustic soda solution from which it can be reprecipitated unchanged. Because of its ferric chloride colouration and its solubility in ice-cold aqueous caustic soda, the possibility of the carbinol (VII) being 1-hydroxy-2-naphthoylacetyl carbinol cannot be ruled out. The product is being studied further to finally decide the position of the acetyl group.

The *diacetate*, prepared by refluxing (VII) with acetic anhydride and pyridine crystallised from alcohol in long colourless needles, m.p. 119°. (Found: C, 67·4; H, 5·1. $C_{16}H_{14}O_5$ requires C, 67·12; H, 4·9%).

The method used by Eistert[8] for converting a diazoketone of the type of (VI) to the coumaranone was then studied, and instead of the coumaranone (I), the carbinol (VII) was obtained. The diazoketone (0·2 g.) was suspended in alcohol (2 c.c.), 2N sulphuric acid (0·2 c.c.) added, and the mixture warmed on the water-bath, when a brisk evolution of nitrogen took place. When nitrogen was no longer evolved, the solution was heated on the water-bath for about 5 minutes (Norit), filtered and cooled, when light brown crystals separated (0·1 g.). The product crystallised from alcohol in light yellow plates, m.p. 121°, identical with (VII).

1-*Hydroxy-2-naphthoylcarbinol* (*IX*).—To a solution of (VII) (0·1 g.) in alcohol (2 c.c.), four drops of concentrated sulphuric acid were added and the solution refluxed on the water-bath for 30 minutes (Norit), filtered and cooled. The yellow crystalline mass, which separated, crystallised from alcohol or benzene in small yellow plates, m.p. 151°, with darkening in colour. (Found: C, 71·3; H, 5·2. $C_{12}H_{10}O_3$ requires C, 71·3; H, 4·9%.) The substance was also obtained by warming a dilute alkaline solution of the acetylated carbinol on the water-bath for 2 minutes, and acidifying. It gives a green colour with ferric chloride and an orange solution in concentrated sulphuric acid.

Acetylation gave the same *diacetate* (VIII) described earlier.

6:7-*Benzocoumaranone* (*I*)

(A) The diazoketone (VI) (0·2 g.) was added slowly with stirring to ice-cold concentrated sulphuric acid (2 c.c.); nitrogen was evolved and the substance slowly went into solution. The brownish orange solution, which had a strong green fluorescence, was kept in the refrigerator for one hour, poured over crushed ice, and ether extracted. The ether extract was washed with ice-cold sodium hydroxide solution, which removed a trace of a colouring matter. The ether layer was washed and dried, and on removal of the ether the residue crystallised from dilute alcohol in shining colourless plates, m.p. 119° (Ullmann, 91–2°; Lanz, 116°; Fries and Ingham, *et al.*, 119°). (Found: C, 78·1; H, 4·5. $C_{12}H_8O_2$ requires C, 78·3; H, 4·3%.) The substance does not give a colour with ferric chloride, and is not soluble in cold aqueous sodium hydroxide; but when slightly warmed it goes into solution with a deep red colour; deep reddish violet flakes then separate (*cf.* Ullmann[2]). It reduces Fehling's solution, and the brownish orange solution in concentrated sulphuric acid shows a bright green fluorescence. The *acetate* prepared by refluxing with acetic anhydride and pyridine, crystallised from alcohol in light brown needles, m.p. 88 (Ingham and co-workers, 85). (Found: C, 74·7; H, 4·7. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%.)

(B) α-Naphthoxyacetic acid was prepared by condensing chloracetic acid and α-naphthol in alkaline solution. The acid chloride, obtained by treatment of the acid (5 g.) with phosphorus pentachloride (5 g.) in benzene, followed by removal of the benzene and phosphorus oxychloride under vacuum on the water-bath, was taken up in benzene (25 c.c.). Aluminium chloride (4 g.) was then slowly added, when the colour of the solution changed from brownish red to green. After heating on the water-bath for 6 hours, the solution which had now become coppery red was poured into ice and hydrochloric acid, and steam-distilled. The white crystalline mass that separated in the distillate was taken up in ether, and the ether removed. The residue (1·2 g.) crystallised from dilute alcohol in colourless shining plates, m.p. 119°, not depressed by admixture with 6:7-benzocoumaranone prepared earlier. The residue in the distillation flask was a deep red resinous mass and could not be crystallised.

SUMMARY

6-7-Benzocoumaranone was first described by Ullmann who prepared it by the cyclization of 2-bromacetyl-1-naphthol and recorded the m.p. 91–2°. Fries prepared it later by the intramolecular acylation of α-naphthoxyacetyl bromide and recorded the m.p. 119°. A compound of the same m.p. prepared similarly from α-naphthoxyacetyl chloride has been considered by

Ingham *et al.*, to be *peri*naphthapyrone. 6:7-Benzocoumaranone, m.p. 119,° has now been synthesised by an unambiguous route, starting from 1-hydroxy-2-naphthoic acid through the intermediate diazoketone, and it has been shown that the product obtained by Ingham *et al.* was 6:7-benzocoumaranone.

We wish to thank Mr. T. S. Gore for carrying out the microanalyses and the Trustees of the Sir Dorab Tata Trust for a scholarship awarded to one of us.

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UMBILICAL PROJECTION† IN FOUR DIMENSIONAL SPACE S_4*

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This paper is an extension of the two papers published by the Author in the *Proceedings of the Indian Academy of Sciences*, Vol. XV, No. 1, Section A, 1942, pp. 16–17; Vol. XXIV, No. 5, Section A, November 1946, *to illustrate the use of* '*Umbilical Projection*' to establish a number of propositions pertaining to the Geometry of Spheres. For this purpose we investigate good many properties of a quadratic W in S_4.

1

Harmonic Inversion w.r.t. a Point and a Prime

1. Let L be a fixed point and l a fixed prime. If P be a point on a line through L cutting l in P_1 and we take P′ on LP such that $(L\,P\,P_1\,P') = -1$, we say that P′ inverts into P w.r.t. (L, l). It is clear from the definition that P inverts into P′, *i.e.*, P, P′ are mutually inverse. L is called the *centre* and l *the prime of inversion*.

If L and l be pole and polar w.r.t.w., we note then the following results:

(i) A prime or plane section of W inverts into another prime or plane section of W meeting them in l. If U be a point on W, U′ the intersection of UL with W, then any prime or plane through U′ inverts into *a prime or plane through U* and *vice versa*.

(ii) l inverts into itself.

(iii) An enveloping hypercone of W with vertex M and section m of W being polar of M as its base inverts into another enveloping hypercone of W with vertex M′ and section m' of W being polar of M′. Hence a pair of inverse point w.r.t. (M, m) inverts into *a pair of inverse points w.r.t.* (M', m').

(iv) If we define the angle between two primes as $\frac{\log r}{2i}$ where r is the cross-ratio of the four primes consisting of the given ones and tangent primes to W through the plane common to them such that $r = -1$ when the given primes are conjugate, *the angle between two primes will be unaltered by inversion.*

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* [Read at the 33rd Session of, the *Indian Science Congress Association*, held at Bangalore, in January 1946. Abstract published in its Proceedings.]

† Baker, H. F., *Principles of Geometry*, Vol. IV. *Representation of a Prime upon a Quadratic*, pp. 36–40.

(v) A line, plane or prime through L inverts into itself. Hence *any plane or prime through a pair of inverse points inverts into itself.*

2.* *Two prime sections a, b of W lie on two hypercones whose vertices V_1, V_2 lying on the polar line of the plane k common to a, b, are harmonically separated by the pairs of points where V_1V_2 cuts W and a, b and also by the pairs of poles A, B of a, b. The polar primes v_1, v_2 of V_1, V_2 are conjugate w.r.t. W, form a harmonic pencil with a, b and are ' primes of inversion ' for a, b with V_1, V_2 as ' centres of inversion '.*

3. Let V_1', V_2', A', B' be the intersections of W with UV_1, UV_2, UA, UB respectively; AB and A'B' meet in a point C, the pole of $V_1'V_2'$ w.r.t. the conic section $UV_1'V_2'$ of W. *Hence the polar prime c of C passes through* V_1', V_2' *and the polar planes of A'B' and AB.*

4. Any line PP' inverts into a line through a fixed point U, where U, P, P' are points on W if we take L, the centre of inversion, on UP or UP'.

5. *If a variable prime cut two given primes at fixed angles it will also cut every prime coaxal with them at a fixed angle.*

6. *All primes of a coaxal system will cut at equal angles two primes which cut two primes of the system at equal angles.*

7. *If a prime section of W touches two other sections; the line of contact must pass through one of the centres of inversion for them.*

8. Given any three prime sections of W; *the six primes of inversion, w.r.t. which the given sections are inverse in pairs, arrange themselves in four coaxal triads and belong to a linear congruence.*†

9. *If each of two primes intersect each of two others at the same angle, a centre of inversion of one pair lies in the common plane of the other pair. For primes cutting two primes at equal angles are conjugate to a prime of inversion.*

In particular, if two prime sections of W touch two other prime sections, a centre of inversion of one pair lies in the common plane of the other.

10. Given four prime sections of W in general, they determine in pairs twelve hypercones whose vertices lie by sixes in four planes each through the

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* *Proc. Lahore Phil. Soc.*, Vol. VIII, August 46, No. 1, p. 59.

† A system of primes passing through a line is said to form a linear congruence.

poles of a triad of them (Article 8) and by threes on sixteen lines. Four such lines pass through each vertex; four lie in each of the four planes; four in each of *eight other planes,* whereof two pass through each of the sixteen lines. Thus the twelve vertices lie by sixes in twelve planes completing a Desmic configuration of three Tetrahedra, each perspective to the other from the vertex of the third that are mutually self-polar.*

11. *Any prime through any one of the eight planes of Article* 10 *cuts all the given four primes at equal angles. Through each plane there pass two primes touching the given sections. Hence there are in all sixteen primes touching the given sections.*

The line joining the point, common to the four primes, to the pole of one of the eight planes w.r.t. one of the given prime sections cuts in points of contact of a pair of tangent sections.

12. *It is easy to see with the help of the eight planes of Article* 10 *that there are sixteen primes cutting any five primes at the same angles.*

13. If P inverts into Q w.r.t. (A, BCDE), Q inverts into R w.r.t. (B, CDEA), R inverts into S w.r.t. (C, DEAB), S inverts into T w.r.t. (D, EABC), then T inverts into P w.r.t. (E, ABCD).

INVERSION W.R.T. A SPHERE *l*

Now on Projection from a point U on W we have in a prime p:

1. P, P′ project into a pair of inverse points w.r.t. a sphere *l* with centre U′.

(i) A Sphere or a circle inverts into a Sphere or a circle coaxal with *the sphere of inversion l.*

A Sphere or a circle through the *centre of inversion U′* inverts into a plane or a line and *vice versa.*

(ii) *l* inverts into itself.

(iii) A pair of inverse points w.r.t. a sphere inverts into a pair of inverse points w.r.t. its inverse.

(iv) If we define the angle between two spheres to be equal to $\frac{\log r}{2i}$ where r is the cross-ratio of the four planes through a tangent line to their common section, two touching the spheres and two touching the circle at infinity, such that $r = -1$ when the spheres are Orthogonal, the angle between two spheres will be unaltered by inversion.

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* *Bull. Cal. Math. Soc.*, Vol. 33, No. 4, 1941, p. 149.

(v) *A pair of inverse points w.r.t. l, a circle or a Sphere orthogonal to l inverts into itself.*

A line or plane through U′ inverts into itself.

2. Given two spheres *a*, *b* their *centres of similitude* V_1, V_2 *are double points of the involution determined by their centres, and their limiting points*; *a*, *b* are inverse w.r.t. two spheres v_1, v_2 having their centres at V_1, V_2 called their *spheres of anti-similitude.* v_1, v_2 are mutually orthogonal and are coaxal with and equally inclined to *a*, *b*.

3. It is easy to notice that the projection of the prime *c* is the *sphere of similitude* for the spheres *a*, *b* having V_1, V_2 as the extremities of a diameter. *This sphere is coaxal with a, b as well as with their centres.*

(i) With the help of Desargue's Theorem for two triangles in perspective we have that *the three spheres of similitude of any three spheres taken in pairs are coaxal. The six spheres belong to a linear congruence.**

(ii) From the property that the corresponding edges of two tetrahedra in perspective meet in a plane, we get that *the six spheres of similitude of any four spheres taken in pairs belong to a linear congruence.** *The ten spheres belong to a linear complex.**

(iii) From the fact that the corresponding edges of two pentads in perspective meet in a prime, we have that *the ten spheres of similitude of any five spheres taken in pairs belong to a linear complex.**

4. Any coaxal system of spheres inverts into concentric one if inversion is effected w.r.t. a limiting point.

5. If a variable sphere cut two given spheres at fixed angles, it will cut also at a fixed angle every sphere coaxal with them.

6. All spheres of a coaxal system will cut at equal angles two spheres which cut two spheres of the system at equal angles.*

7. The line of contact of a sphere touching two others passes through either centre of similitude.*

8. Given three spheres, the six centres of similitude arising from these lie by threes on four lines in a plane. *The six spheres of anti-similitude arrange themselves by threes into four coaxal families which are orthogonal to the family of spheres orthogonal to the given three and hence they belong to a linear congruence.*

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* Coolidge, *A Treatise on the Circle & the Sphere*, Chapt. 5.

9. If each of two spheres intersect each of two others at the same angle a centre of similitude of one pair lies in the radical plane of the other pair.* In particular if two spheres touch two others a centre of similitude of one pair lies in the radical plane of the other.*

10. Given four spheres in general, they determine in pairs twelve centres of similitude. These lie by sixes in four planes each through three centres of given spheres and by threes on sixteen lines. Four such lines pass through each centre of similitude, four lie in each of the four planes and four in each of eight other planes, whereof two pass through each of the sixteen lines. The centres of similitude lie by sixes in twelve planes completing a desmic configuration of Stephanos.*

The twelve spheres $v_1 (i = 1, 2 \ldots . 12)$ *of antisimilitude belong to a linear complex and group into three tetrads such that a sphere of one and that of a second are coaxal with a sphere of the third tetrad. There are sixteen such coaxal families which by fours belong to twelve linear congruences* u_j $(j = 1, 2 \ldots . 12)$. u_j *also group into three similar tetrads such that a linear congruence from one and that from a second have a family common with a linear congruence from the third tetrad. The sixteen families arising from them are orthogonal by fours to the twelve spheres* v_i *and each of these families is orthogonal to a family of the former sixteen. Each* u_j *is orthogonal to six* v_i *and each* v_i *to six* u_j. *Every sphere belongs to four families.*

11. *There are eight families of spheres that cut four given spheres at equal angles.* Hence there are sixteen spheres, two from each family, that touch the four spheres.

The line joining the radical centre of the four spheres to the pole of one of the eight planes of Article 10 w.r.t. one of the spheres cut it in the points of contact of a pair of tangent spheres.*

12. There are sixteen spheres that cut any five spheres in general at equal angles.*

13. *Given five mutually orthogonal spheres* l_i $(i = 1, 2, \ldots 5)$; *if P inverts into Q w.r.t in* l_1, *Q inverts into R w.r.t.* l_2, *R inverts into S w.r.t.* $T l_3$, *S inverts to T w.r.t.* l_4, *then T inverts into P w.r.t.* l_5.

II

MISCELLANEOUS

1. Given a self-conjugate pentad ABCDE for W, A′B′C′D′E′ be the pentad inscribed in W in perspective with ABCDE from a point U of W.

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† Coolidge, *Loc. cit.*

The traces of the given pentad on the tangent prime at U are ten points and ten lines constituting a self-polar set and the traces of the pentad formed by the tangent primes at A', B', C', D', E' are the same as those of the given pentad.

Definition.—A plane and a line will be said to be *conjugate* when the polar line of the plane intersects the given line (*in the pole of the prime that contains the given plane and the polar plane of the given line*).

2. Given a simplex such that each of its planes is conjugate to the opposite line; *the reciprocal simplex w.r.t. W is also of similar character. The two simplexes are easily seen to be in perspective, from a point which taken with the five vertices of the given simplex constitute such a set of six points that the plane determined by any three of them is in bi-involution with the plane determined by the other three and the line joining any two of them is conjugate to the prime determined by the other four.*

3. Let *ab*, *cc'* be pairs of coaxal primes forming a harmonic pencil, U be a point on the section *c* of W, P on the section *c'*, if UP cuts *a*, *b*, in Q, Q' we have (UP, QQ') = − 1, *i.e.*, Q, Q' are conjugate points for W.

(i) Hence *the polar prime of Q passes through* Q' and is conjugate to *a*.

(ii) If the given primes *a*, *b* be conjugate, *i.e.*, A, pole of a lies in *b*, and UA cut W in A', *b* in A_1, we shall have ($UA_1A'A$) =, − 1, A' *must lie then on the prime c'*.

(iii) *The poles of the primes also form a harmonic range, the pole of c being in the tangent prime at U.*

4. Given four primes *a*, *b*, *c*, *d*; let A, B, C, D be their poles respectively, UA, UB, UC, UD meet *a*, *b*, *c*, *d* in A', *B'*, *C*,' *D'* respectively and W in A",B",C",D". Then the primes A"B"C"D", ABCD and A'B'C'D' are coaxal. If their common place be *k*, the prime *k*U will be harmonic conjugate of the prime A"B"C"D" w.r.t. the primes ABCD and A'B'C'D'. *k* is the plane where AB meets A'B', etc.

5. If a plane section *s* of W through U be conjugate to a prime *a* and cut its section in points forming a harmonic range on *s* with another pair of points on it; *any prime through the 2nd* pair of points will be conjugate to *a*.

On projection from U in the prime *p* we have:

1. *The centres of the spheres through an orthocentric set of five points also form an orthocentric set.*

Definition.—A circle and a pair of points will be said to be conjugate to each other when the foci of the circle are concyclic with the given pair of points, *in which case the circle, for which the given pair of points are foci, shall be cospherical with the given circle.*

2. Given five spheres such that the circle common to two of them is conjugate to the pair of points common to the other three; *the centre of one joined to the radical centre of the other four passes through a fixed point, i.e., the two pentads formed by the centres and the radical centres are in perspective. The sphere orthogonal to four of them and the fifth are coaxal with a fixed sphere whose centre is the fixed point. The latter sphere along with the given five constitute a set of six spheres such that the circle orthogonal to any three of them is in bi-involution with the circle orthogonal to the other three and the line joining the centres of any two of them contains the radical centre of the remaining four. The same shall hold for the five spheres orthogonal to the given five along with this sphere .*

3. (i) If a variable sphere is cut by one sphere orthogonally and the other in a great circle, the locus of its centre is another sphere which we may call as the *radical sphere** of the two spheres.

(ii) *If the given spheres are orthogonal, their radical sphere passes through their centres.*

(iii) *The centre of the radical sphere of two spheres is the mid-point of the join of the centres of the given spheres.**

4. The sphere orthogonal to four spheres, and the sphere which cuts all of them in great circles are coaxal with the sphere determined by the centres of the given four and *orthogonal to their spheres of similitude* (*Article* 3 (ii) *Section* I).*

*The sphere through the centre of the given spheres is the radical sphere of the sphere cutting them all in great circles and the sphere orthogonal to them all.**

5. *The diameter of one sphere cuts another orthogonal to the first in a pair of inverse points w. r. t. to the second.*

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* Coolidge, *Loc. cit.*

A NOTE ON THE AROMATIC PRINCIPLE OF *TYLOPHORA INDICA* (BURM. f.) MERR.

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THE previous examination of *Tylophora indica* (Burm. f.) Merr. (syn. *asthmatica* Wight and Arn.) by Hoopers'[1] or by Ratnagiriswaran and Venkatachalam[2] does not record the presence of any aromatic constituent, though the plant as a whole, particularly the root, has a pleasant characteristic odour resembling somewhat that of vanillin.

It is now found that when the air-dried root powder is subjected to steam distillation, a colourless crystalline solid along with a little oil distils over, the yield being 0·18 per cent. But a better yield, 0·26 per cent., is obtained, if the material were to be first percolated with alcohol, and the extract, after removal of the solvent, is distilled with steam. From the distillate the crystalline solid is filtered, and from the mother-liquor the oil is recovered through ether extraction.

The solid, which forms 85 per cent. of the total essential oil, is sparingly soluble in cold water, more so in hot water and readily in organic solvents. From dilute alcohol it crystallises in rectangular plates, melting at 42°. It dissolves readily in dilute sodium hydroxide: in aqueous alcoholic solution it produces a deep purplish-red colour, indicating its phenolic nature. The formation of the phenyl hydrazone, m.p. 137–38°, and the oxime, m.p. 138°, shows the presence of an aldehyde group. These properties, as also its composition ($C_7H_5O_2 \cdot OCH_3$), reveal the identity of the compound as *p*-methoxy salicylaldehyde (4-O-methyl resorcylic aldehyde), and this has been confirmed by comparison with an authentic sample kindly supplied by Prof. T. R. Seshadri of the Andhra University.

p-Methoxy salicylaldehyde has been reported to be present in the roots of some plants belonging to the family Asclepiadaceæ, namely, a species of *Chlorocodon*,[3] *Decalepis hamiltonii* Wight and Arn.,[4] and *Hemidesmus indicus* Br.[5] Its presence in *Tylophora indica* is a further addition.

The aldehyde has a sweet and agreeable odour, a mild pungent taste and is said to possess powerful bacteriostatic properties. It has, therefore, been suggested to be a good natural preservative for the preservation of food.[6]

The oily part of the essential oil, after the removal of any dissolved *p*-methoxy salicylaldehyde by treatment with dilute sodium hydroxide, is a viscous oil having the same characteristic smell as that of the roots. On standing it deposits a small amount of a waxy solid. On account of the low yield of these substances, they have not been characterized.

The stems and leaves of the plant also yield the same essential oil but in smaller amount.

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INTERACTION OF NITROGEN AND SULPHUR UNDER SILENT ELECTRICAL DISCHARGE: PRODUCTION OF A REVERSE CHANGE

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Previous results[1] for the behaviour under electric discharge of phosphorus films towards nitrous oxide, air and nitrogen showed very marked and sudden changes in the conductivity during the removal of nitrogen by phosphorus. It was of interest therefore, to investigate the corresponding reaction with sulphur. Anticipated by Joshi as possibly associated with the production under silent discharge, of a periodic effect in the interaction of nitrous oxide with hydrogen and decomposition of nitrogen dioxide,[2, 3] the present work has revealed a spontaneous *self-reversal* in the over-all direction of a discharge reaction. This *reversal* is not a transient or spurious effect; but a reproducible characteristic under well-defined conditions; and shown by markedly synchronous changes in the gas pressure (p), the discharge current (i) and nature of the corresponding glow, which do not appear to have been recorded in the literature.

Experimental

The general apparatus and the electrical circuit used were essentially the same as described elsewhere.[1] The discharge vessel consisted of two soft glass tubes fitted co-axially, as in a Siemens' type ozoniser, with a rubber greased ground joint. The inner tube and the one surrounding the outer tube were filled with a moderately concentrated salt solution and served as two terminals of the ozoniser. The temperature of the system was kept constant by circulating water at a slow but constant rate through a water jacket enclosing the ozoniser. A uniform and thin film of sulphur was deposited on the outer surface of the inner electrode by coating it with a concentrated solution of sulphur in carbon disulphide. The tube was fitted in the ozoniser system and the solvent was removed completely by evacuating it on the Töpler. The main experiment was commenced only when the system maintained a satisfactory vacuum at least for 24 hours.

Nitrogen was obtained from a commercial cylinder. The gas was bubbled slowly through a series of traps filled with a freshly prepared solution of alkaline pyrogallol and was led over heated copper turnings to remove traces of oxygen. It was dried carefully by streaming it slowly through a train of tubes containing phosphorus pentoxide and calcium chloride and admitted to the ozoniser at a desired pressure.

The A.C. output of 50 cycles frequency, obtained from a rotary converter worked off 220 volt D.C. mains, was fed to the primary of a step up transformer. Its secondaries were connected to the inner and outer electrodes, *i.e.*, the H.T. and L.T. terminals of the ozoniser. The potential applied to the ozoniser V, expressed in kilo-volts (r.m.s.) kV, was calculated from the primary potential and the step-up ratio of the transformer. The discharge current i was measured by a Weston's moving iron A.C. milliammeter or an oxide rectifier type Cambridge A.C. micro-ammeter connected between the earth and the low-tension terminal of the ozoniser.

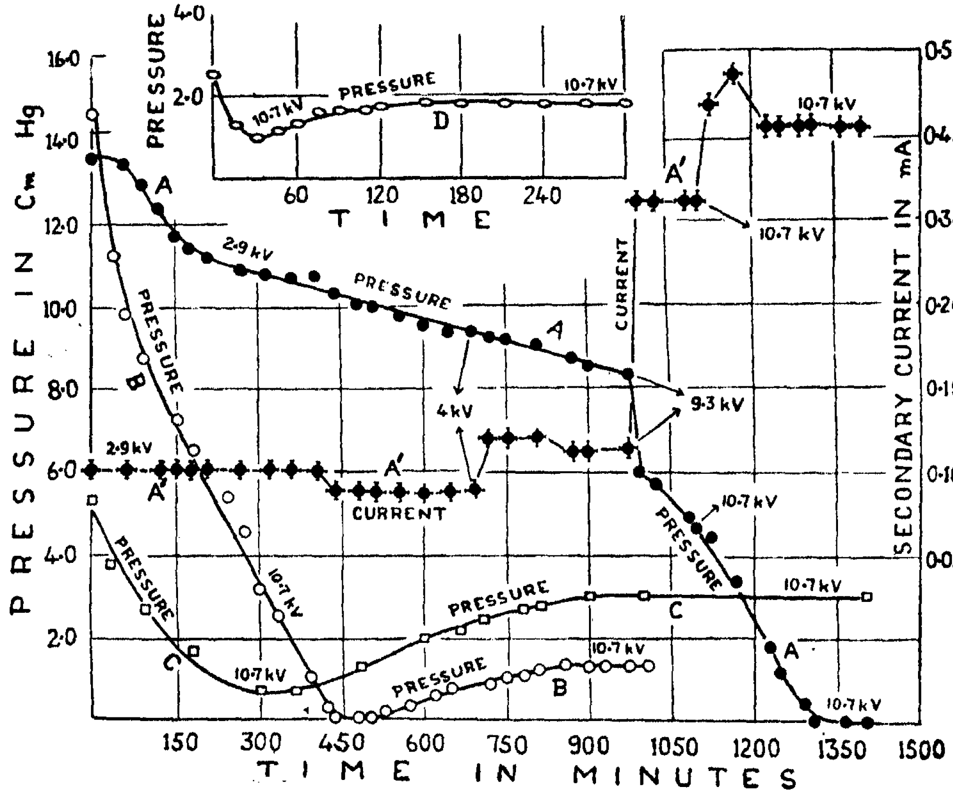

FIG. 1. Pressure, Current Variation during S—N$_2$ Reaction at 2·9, 4, 9·3, 10·7 kV. 50 Cycles Sec.$^{-1}$

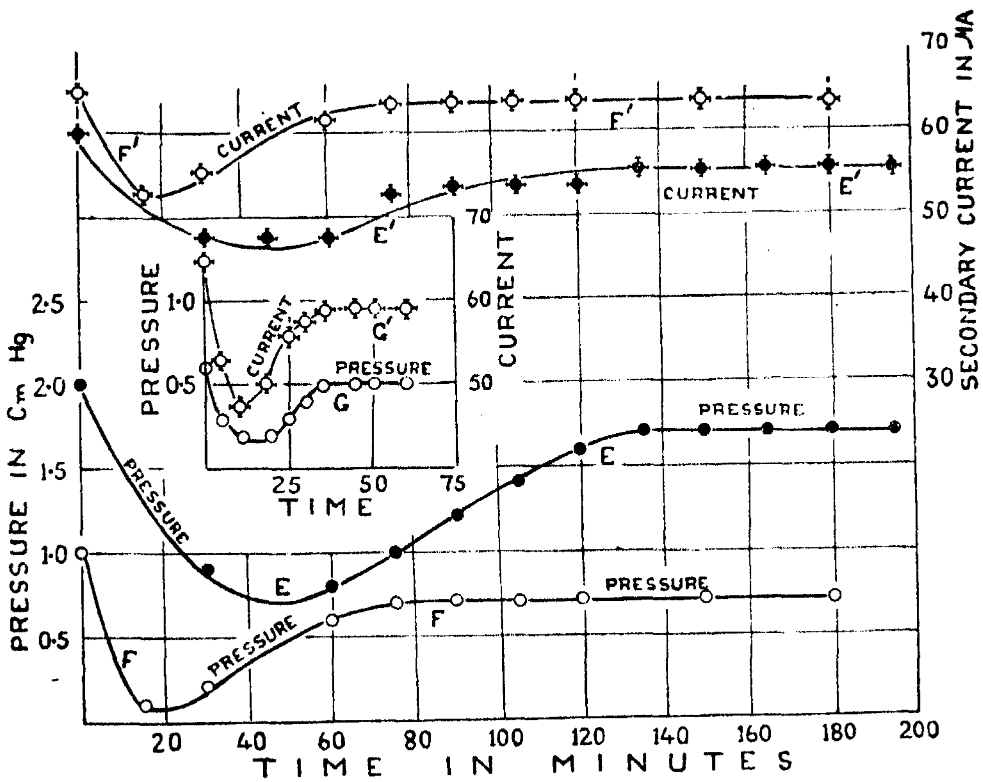

FIG. 2. Pressure, Current Variation during S—N_2 Reaction at 10·7 kV. 50 Cycles $Sec.^{-1}$

The ozoniser was filled with purified nitrogen at different initial pressures and subjected to discharge at V varied in the range 2 to 11 kV of 50 cycles frequency; a fresh film of sulphur was used in each experiment. The progress of the reaction was followed by a time to time determination of the pressure of the reaction mixture at constant volume and also the corresponding discharge current i flowing through the ozoniser at a given applied V.

Figs. 1 and 2 illustrate the results obtained for the variation of p and i during the interaction of sulphur and nitrogen under the experimental conditions mentioned above. The products of the reaction were analysed when p and i reached the minimum stage. The discharge was discontinued at this stage; the film on the outer surface of the inner electrode was removed and analysed for the presence of sulphur nitride. Fig. 3 shows the time required for (*a*) the initial diminution of p to a minimum; (*b*) its subsequent increase to a maximum stage due to *reversal*; and (*c*) that for the total change (*a*) + (*b*). This as also the relative pressure recovery $100 \times \frac{\text{Final } p}{\text{Initial } p}$, serve

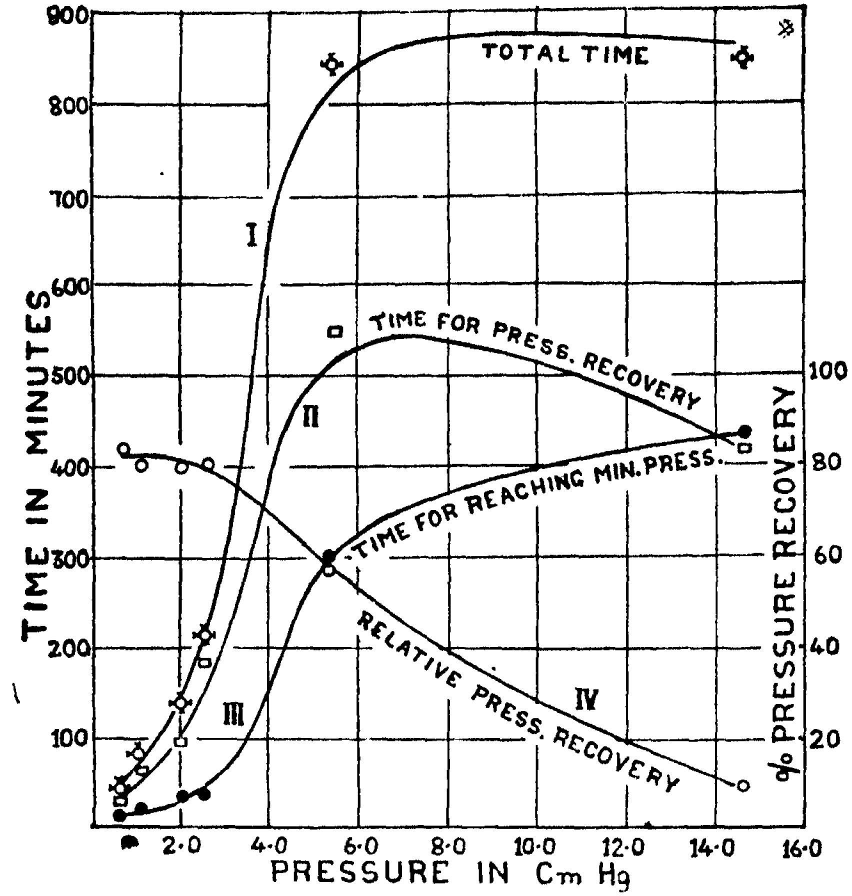

FIG. 3. Pressure, Time Variation during S—N_2 Reaction at 10·7 kV, 50 Cycles Sec.$^{-1}$

as a measure of the velocity of the reaction at different initial pressures of nitrogen and a constant applied V.

DISCUSSION OF RESULTS

As with phosphorus films, oxidation under discharge of sulphur by air dried carefully, was found to set in only at a characteristic 'threshold potential' V_m, as located by an incipient current rise and pressure change. Much greater V_m than in the case of phosphorus was, however, required in the sulphur-nitrogen reaction due, in part, to the comparatively greater dielectric strength of sulphur. The pressure-time curves A–G in Figs. 1 and 2 show that during the initial stage of the reaction, *p* decreases continuously to a minimum and on continued exposure to discharge (at a constant applied V), increases slowly to a constant maximum; after this, no further pressure change occurs on continuing the discharge for an appreciably long time. The total time for the reaction, *i.e.*, when p reached its minimum on the time axis and then increased to a constant maximum during the *reversal* (see curve 1 in Fig. 3); and also the average time-rate of the pressure change increased with V and $1/p$. Thus *e.g.*, at 10·7 kV and an initial pressure corresponding to 14·6 and 5·6 cm. of nitrogen (curves B and C in Fig. 1) p reached the minimum in about 450 and 300 minutes respectively. This is in agreement with Joshi's deduction that the 'threshold potential' V_m increases with p and that the velocity of a discharge reaction depends on $V-V_m$.[4,5,6] Furthermore, curve A in Fig. 1 shows that with 13·6 cm. of nitrogen and V varied from 3 to 11 kV, the pressure decreased to a minimum in about 1,300 minutes. This slow pressure diminution, indicative of a reduction in the over-all velocity of the reaction, was more conspicuous when V was nearer to V_m. Thus at 2·9 kV, only 30 per cent. of the pressure change occurred in about 675 minutes and the rate of pressure diminution increased as V was raised progressively to 10·7 kV. Detailed experiments showed that the *reversal* of p was more pronounced at low initial pressures of nitrogen and was accompanied by a synchronous variation of the discharge current i (curves E–G and E′–G′ in Fig. 2). The percentage restoration of both the above quantities, at a given V, increased markedly as the initial pressure of the gas was reduced progressively (see curve IV in Fig. 3). Thus *e.g.*, at 10·7 kV and 14·6 cm. of nitrogen (curve B in Fig. 1), p became negligibly small in about 450 minutes and increased on continued exposure to discharge to a maximum corresponding to 1·3 cm., *i.e.*, to about 9% of its initial value (see curve IV in Fig. 3). Compared with this, the relative recovery of p (due to *reversal*) was much greater *viz.*, about 83% when the pressure of nitrogen was lower, *i.e.*, 2·0 cm. Hg (curve IV in Fig. 3 and curve E in Fig. 2).

Also, the current i showed a remarkably synchronous variation with p; it decreased from the initial 60 to 47 μA and increased again to 55 μA, *i.e.*, to about 90 per cent. of the original conductivity (curve E′ in Fig. 2). Results for the sulphur-nitrogen reaction at 10·7 kV, but lower initial pressures of nitrogen were found to be on the whole similar to those mentioned above (curves F–F′ and G–G′ in Fig. 2). The variation of i was less pronounced at high initial pressures of nitrogen. This was partly due to the use of a less sensitive indicator then available for these measurements. Curve A′ in Fig. 1, however, shows that at 13·6 cm. of nitrogen, i either remained sensibly constant or decreased at a given V when p decreased continuously. It, however, increased to a higher value on increasing V successively and was constant so long as the applied V was also constant. During this, it was observed that the intense violet appearance of the glow faded gradually with the decrease of p and i; it disappeared almost completely as both the above quantities reached the minimum and was not observed even during their *reversal* on continued exposure to discharge.

It is interesting to point out that if after the attainment of the constant maximum p (due to *reversal*) the residual gas was töplered out completely and the system re-excited at V applied previously, an increase of pressure ensued. Thus, *e.g.*, at 10·7 kV and 5·6 cm. of nitrogen (curve C in Fig. 1), p decreased to 0·7 cm. and increased again (on continued exposure to discharge) to 3·0 cm. in about 900 minutes. The experiment was discontinued at this stage. The ozoniser was evacuated on the Töpler and the discharge was switched on at the original applied 10·7 kV. It was now seen that p increased slowly and reached a constant stage corresponding to about 0·6 cm. in 130 minutes. On further evacuation on the Töpler and exposure to discharge under constant experimental conditions, the pressure increased once again but on the whole more slowly than before. Thus, after the second evacuation of the residual gas, 160 minutes were required for the same amount of pressure change, *i.e.*, 0·6 cm. rise of p. It is significant to observe that such a reversal of pressure after the attainment of minimum p, which (latter) in the case of phosphorus corresponded to practically zero pressure, was never observed in the phosphorus-nitrogen reaction under generally identical conditions even though the exciting potential was increased considerably.

Newman[7] found that certain elements deposited as thin films over the cathode, absorbed nitrogen rapidly under the discharge. With phosphorus, sulphur and iodine the absorption was most pronounced and the gas was not reliberated even on heating the discharge tube, which he attributed to the formation of a stable chemical compound. The general resemblance of the S–N_2 reaction under electric discharge as shown by the initial time-variation of p, with that when phosphorus was used instead, is suggestive. The removal of nitrogen by phosphorus was, however, attributed chiefly to the formation of a chemical compound since no *reversal* of pressure was observed and the termination of the reaction was characterised by a sudden and large drop of i to a stationary value when p became negligibly small. During the course of the reaction, the colour of the phosphorus film changed from yellowish white to dark brown and the reaction products revealed the presence of phosphorus nitride. In the present series of experiments the analysis of the products of the reaction indicated the formation of sulphur nitride. Judged by the time-rate of the variation of p, the 'clean up' of nitrogen by phosphorus was comparatively more rapid than that by sulphur.

Thus, at 4 kV and 11·3 cm. of nitrogen p became negligibly small in about 330 minutes in the P–N_2 reaction. Using almost similar pressure, *i.e.*, 14·6 cm. of N_2 and a much higher applied V, namely 10·7 kV, only 80% of the pressure change occurred in 330 minutes in the latter case (curve B, Fig. 1).

Kohlschütter and Frumkin[8] obtained phosphorous nitride by passing an electric discharge through a mixture of phosphorus vapour and nitrogen. No data are, however, available for the formation of sulphur nitride as a result of the interaction of sulphur and nitrogen under the discharge. The detection of sulphur nitride in the products of the reaction in the present series of experiments is therefore, interesting.

Three volatile modifications of sulphur nitride are known; of these, nitrogen tetrasulphide (N_4S_4) is comparatively more stable and obtained as a yellowish brown solid at ordinary temperature. The other two varieties, *viz.*, nitrogen persulphide (NS_2) and nitrogen pentasulphide (N_2S_5) were obtained by Usher[9] and Muthmann[10] by heating N_4S_4 with sulphur and carbon disulphide respectively. Both the above compounds are liquids with a characteristic deep red colour and are easily decomposed at ordinary temperature into N_4S_4 and sulphur. It is, therefore, suggested that the reaction products obtained under the discharge in the present experiments consisted chiefly of nitrogen tetrasulphide, as the formation of a liquid product was not detected at any stage during these experiments.

It is instructive to compare at this stage the relative stability of phosphorus nitride and sulphur nitride. Phosphorus nitride (P_3N_5) is fairly stable at ordinary temperature and decomposes only above 910°[11]; its heat of formation, using ordinary phosphorus was found by Stock and Wrede[12] to be + 81·5 K. Francis and Davis[13] observed that nitrogen tetrasulphide (N_4S_4) decomposes almost completely at 185°. Berthelot and Vieilli[14] found the compound to be *endothermic* having a heat of formation − 127 K. This shows that sulphur nitride is comparatively more unstable than phosphorus nitride.

The observed *reversal* of pressure accompanied by the synchronous time-variation of i (Figs. 1 and 2) may be attributed to the formation and subsequent decomposition of sulphur nitride and/or the adsorption and desorption of the gas on the sulphur film under the discharge.

In a theory of the newly discovered *Joshi-effect*, *viz.*, an instantaneous and reversible photo-diminution $-\Delta i$ of the discharge current i in chlorine and other gases and vapours, Joshi[15] has postulated the formation of a 'variable adsorption layer' derived in part, from the wall adsorption of the ions and excited molecules under the discharge. The formation of this layer would alter the electrical capacity of the annular space in the ozoniser and therefore, of the corresponding discharge current i at the given applied potential V. Furthermore, Joshi[16] has argued that a decrease of i in the ozoniser discharge can originate from (1) a decrease of C_w, the combined capacity of the walls and C_g, the capacity associated with the gas phase. This last may be regarded as shunted by an ohmic resistance R_g under discharge due to a given exciting potential V. $1/R_g$ is the conduction current determined by the average velocity and number of ions per c.c. *Ceteris paribus* the conduction current should ordinarily increase by decreasing the gas pressure. The decrease of the current with p and its increase during the latter stage characterised by pressure *reversal* cannot, therefore, be attributed to the variation in ohmic or the conduction part of the current, $1/R_g$. The observed variation of i may, therefore, be due to a change in C_w and/or C_g. Since $C_w = \dfrac{0 \cdot 2416\, lK}{\log 10 \dfrac{r_1}{r_2}}$, where l is the length of the ozoniser, r_1 and r_2 the radii of the outer and inner tube (constituting the ozoniser) and K the dielectric constant of the wall material; reduction in K should produce a corresponding decrease of C_w. Applying the Maxwell relation $\mu^2 = K$, data for the refractive index of sulphur and nitrogen tetrasulphide[17] (μ being $1 \cdot 998$ and $1 \cdot 908$ respectively), show that the dielectric constant of sulphur is greater than that of N_4S_4. Assuming that r_2 does not change appreciably during the course of the reaction, the synchronous diminution and *reversal* of p and i, characteristic of the formation and subsequent decomposition of nitrogen tetrasulphide may, therefore, be due to the corresponding variation of C_w. The above suggestion can only be a partial explanation since the observed current changes are far larger than the corresponding difference in the dielectric constants. Furthermore, C_g the capacity associated with the gas phase, should vary synchronously with the gas pressure p. The diminution of i with p and its subsequent increase during the *reversal* of pressure may, therefore, be anticipated.

The disappearance of the glow when p and i reach the minimum stage and its subsequent non-observation during their *reversal* in the latter part of the S–N_2 reaction is explicable on the assumption that during the initial stage of the reaction, the appearance of the intense violet glow may be due to the excitation of sulphur. With the replacement of sulphur by another emitter, *viz.*, N_4S_4, p decreases and the glow fades and disappears almost completely at the minimum p stage. The non-observation of the glow at this stage and also during the *reversal* of p suggests that the excitation potential of N_4S_4 may be greater than that of sulphur. Alternatively, the glow may be due to the excitation of sulphur by active or atomic nitrogen produced under the discharge. Production of active nitrogen under 'silent discharge' has been observed, it would appear, for the first time by Joshi and Purushottam.[18] As p decreases the net concentration of atomic + active nitrogen falls and at minimum p it may not be sufficient to excite sulphur; the glow, therefore, fades and disappears almost completely. If during the *reversal* of p, indicative of the desorption of nitrogen and/or the decomposition of N_4S_4, the liberated gas is in the atomic state or/and 'active', a reappearance of the glow should follow. Its non-observation during the *reversal* does not, therefore, support the latter assumption. It may, however, be assumed that during the initial stage of pressure reduction, a protective film due to the formation of N_4S_4 and/or adsorption complex of sulphur and nitrogen (having properties similar to N_4S_4) is formed on the surface of the sulphur deposit; the formation of this film may inhibit the excitation of sulphur and consequently the appearance of the glow even during the *reversal* of p.

It is suggested that like its formation, the decomposition of sulphur nitride may depend on $V-V_m$. This is illustrated by the general result that at a constant applied V and high initial pressure of nitrogen, the rate of change in p indicative of the formation and decomposition of sulphur nitride is comparatively slow, as V_m increases with p and $V-V_m$ is not large. p reaches the minimum rapidly and its relative recovery due to *reversal* is more pronounced as the initial pressure of N_2 is reduced progressively (Figs. 1 and 2). The constant maximum stage reached during the *reversal* may be attributed to the attainment of a steady state between the liberated gas and the undecomposed film. This is supported by the observation that on evacuating the ozoniser after p has reached the constant maximum due to *reversal* and re-exposing the film to discharge at a constant V in vacuum, an increase of p results. Relatively, however, the rate of increase of p falls on evacuating the system successively and re-subjecting the film to discharge, the exciting potential being kept constant throughout the series.

Grateful thanks of the authors are due to Professor S. S. Joshi, D.Sc. (London), F.A.Sc., F.N.I., for suggesting the problem and for valuable guidance during the work.

SUMMARY

Results are given for the interaction of sulphur films with nitrogen at various initial pressures p (2–15 cm. Hg) and excited in the range 3 to 11 kV (50 cycles). The occurrence of the reaction only above a minimum

'threshold potential' V_m and the dependence of its velocity, at a given V, on $V-V_m$ are in accord with Joshi's concept of the fundamental importance of V_m in discharge reactions.[4, 5, 6] With a fresh film of sulphur, p and i decrease progressively, reach a minimum and increase again to a constant maximum stage almost synchronously on continued exposure to discharge. The *reversal* of p and i is more pronounced as V and $1/p$ are increased. The formation of sulphur nitride is observed. The time variation of p and i suggest that the 'clean-up' of nitrogen is due to the formation of nitrogen tetrasulphide and/or adsorption complex of sulphur and nitrogen. The disappearance of the glow at the minimum p stage and its non-observation during the *reversal* is attributed to the formation of a protective film of N_4S_4 or/and adsorption complex on the sulphur film under the discharge.

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ELASTIC BEHAVIOUR OF QUARTZITE AND FUSED QUARTZ

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1. Introduction

Quartz occurs in Nature in various forms, chiefly in the crystalline state, and in the form of sand stones or quartzites. In the quartzites, the grains of quartz appear to be cemented together by infiltration of soluble silica. When the sections are examined microscopically, the quartz grains can usually be seen in the outline within an envelope of unfiltered and crystallized silica. In some cases the quartz grains are recrystallized.

The present experimental investigation of the elastic behaviour of quartzite and of fused quartz is taken up to find, in the first instance, whether the former shows elastic isotropy or anisotropy. If the minute crystals composing the bulk of quartzite are oriented in a perfectly random manner, it is natural to expect a quasi-isotropic elastic behaviour in it. If, on the other hand, there is any preferred orientation, it would probably show a crypto-crystalline behaviour.

Considerable work was done by Ide[1] on geological rocks in general and quartzites in particular in connection with the interpretation of observed elastic velocities in the rocks of the earth's crust to infer its structure at inaccessible depths. His results are also given later in the paper for comparison.

The structure of the sample of quartzite under investigation shows an obvious non-uniform grain in the medium, with crevices and probably air cavities here and there.

2. Experimental

The method of investigating the elasticity of the sample is by sending an ultrasonic wave, using the wedge method developed in the Andhra University laboratories.[2] Sections parallel to three orthogonal directions are cut from the sample of the rock and ground to plates of different uniform thicknesses, and placed in contact with a quartz wedge, driven by an ordinary Hartley oscillator of variable frequency, thus providing a continuous range of ultrasonic oscillations. When the frequency of the piezo-electric oscillations coincides with the natural frequency (or a harmonic) of the plate itself, it will be thrown into resonance vibrations. The resonance point is found by using the Debye-Sears' method of detecting ultrasonic waves in a liquid.

3. Experimental Observations and Results

Before going into the quantitative results, a particular observation may be noted here. Considerable difficulty is experienced in sending an ultrasonic beam through the quartzite plate and the diffraction pattern is relatively weaker with a quartzite plate than with a similar plate of fused quartz. A tentative explanation of the fact may be found in the non-uniform structure of the quartzite, and also because of the presence of cracks and cavities in the medium. Scattering of the elastic wave due to single grains or groups of grains on the one hand and the absorption of energy by the possible air cavities on the other might result in considerable weakening of the emergent ultranosic beam. It is pertinent to point out here that Rayleigh[3] has actually given a formula for the scattering of sound energy by each particle, namely,

$$\frac{\mathrm{S{\cdot}A}}{\mathrm{I{\cdot}A}} = \frac{\pi \mathrm{T}}{\mathrm{R}\lambda^2}\left[\frac{\delta \mathrm{K}}{\mathrm{K}} + \cos\theta\cdot\frac{\delta\rho}{\rho}\right]$$

where S.A and I.A are the scattered and incident amplitudes, T, the volume of the grain, λ the wave-length, K the elasticity of the medium, δK the difference in elasticity between the particle and the medium, ρ the density of the medium, θ the angle between the direction of observation and that of the incident wave, R the distance of the particle from the point of observation. In this case, the difference in elasticity arises from both the different grain orientations and the structure of the medium.

The results of the investigation on quartzite and fused quartz are given in the following table. The three Orthogonal directions are taken as OX_1, OX_2, OX_3. The elastic constant is given in units of 10^{11} dynes/cm.^{2}

TABLE I

	No.	Description	Thickness in m.m.	Density g/cm.^{3}	Fundamental frequency in mc./sec.	Velocity in metres/sec.	Effective elastic constant C'_{11}
Quartzite	1	$\|^l$ to OX_1 ..	2·59	2·651	0·970	5024	6·69
	2	do ..	2·15	2·616	1·178	5065	6·71
	3	do ..	1·92	2·590	1·323	5 81	6·68
	4	$\|^l$ to OX_2 ..	2·09	2·590	1·215	5077	6·68
	5	do ..	1·76	2·582	1·433	5099	6·71
	6	do ..	1·69	2·630	1·493	5047	6·70
	7	$\|^l$ to OX_3 ..	2·21	2·620	1·140	5039	6·66
	8	do ..	2·25	2·588	1·125	5086	6·70
	1	Fused quartz plate	1·51	2·210	1·662	5019	5·57

Average density of quartzite determined by using
  a lump of it .. .. .. $2{\cdot}646$ g/cm.^{3}
Average velocity in quartzite .. .. 5065 metres/sec.
Average elastic constant .. .. $6{\cdot}69 \times 10^{11}$ dynes/cm.^{2}

The experimental values of Ide are given in the following table for comparison.

TABLE II

Material	Specimen No.	Large cylinders		Small cylinders	
		Density g/cm.^{3}	Velocity metres/sec.	Density g/cm.^{3}	Velocity metres/sec.
Pensylvania	1	2·66	5184	2·66	5033
	2	2·65	4895	2·67	4696
	3	2·64	4647	2·66	5003

The Young's modulus E and the rigidity modulus n for fused quartz fibres are given in standard Tables. Taking the average of values given namely, $E = 5{\cdot}3 \times 10^{11}$ and $n = 3{\cdot}0 \times 10^{11}$ and using the well-known formula applicable to isotropic bodies, we have

$$(c_{11})_{iso} = \frac{n\,(4n - E)}{3n - E} = 5{\cdot}43 \times 10^{11}.$$

This result is in good agreement with the observed value for the fused quartz plate, namely $5{\cdot}57 \times 10^{11}$.

4. DISCUSSION OF RESULTS

From Table I, it is clear that the velocity of the elastic wave is nearly the same along the three directions X_1, X_2 and X_3 within experimental errors. It is interesting to see that the above velocity is nearly equal to that of a sound wave in a fused quartz plate. The difference in the elastic constants in the two substances arises on account of the large difference in the densities. It can also be seen from Table I that the elastic constants in quartzites are the same in all the three directions X_1, X_2 and X_3.

The density differences from plate to plate of quartzite might be largely due to local variations of the irregular grain structure.

In view of the above results in quartzite itself, it is legitimate to conclude that at least as far as elasticity is concerned, quartzite possesses what might be called a quasi-isotropic structure. The conclusion is further strengthened by comparing the velocity in quartzite with that in fused quartz which is itself an isotropic medium. From this particular similarity, it is also reasonable to infer that the orientation of grains in quartzite is quite random.

SUMMARY

The velocities of an ultra-sonic wave are determined along three orthogonal directions in quartzite and from them the effective elastic constants are calculated. For comparison, the same have been determined in a plate of fused quartz. The velocities and the elastic constants in quartzite come out to be the same in the three directions. Further, the velocity in fused quartz is found to be very nearly equal to that in quartzite. It is therefore inferred that the orientation of quartz grains is random in quartzite.

In conclusion the author wishes to express his thanks to Prof. S. Bhagavantam under whose guidance this work was done.

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CONSTITUTION OF OROXYLIN-A AND SYNTHESIS OF ITS DIETHYL-ETHER

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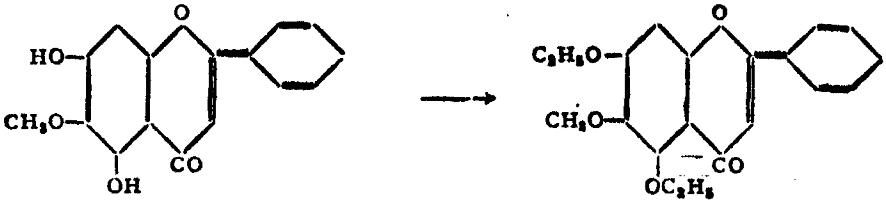
The name oroxylin-A was given by Shah, Mehta and Wheeler[1] to a substance that was isolated from the root bark of *Oroxylum indicum* having a melting point of 231–32°. It was considered to be a monomethyl ether of baicalein and based on its properties and colour reactions it was given the constitution of baicalein-6-methyl ether (I). In the root bark it was associated with baicalein which however could be removed easily because of its instability in alkali.

The stem bark of the same plant was studied in detail by Bose and Bhattacharya.[2] They showed that the colouring matter called oroxylin by earlier workers consisted of a mixture of three substances. They could isolate in a pure condition chrysin and baicalein and definitely show the presence of the 6-methyl ether of baicalein though they could not separate it from the mixture. From certain considerations which were not mentioned they inferred that this methyl ether should have a melting point lower than 230°. After removing baicalein they subjected the remaining mixture to detailed fractionation and found that a very small fraction melting at 220–23° was the nearest approach to the 6-methyl ether of baicalein (Found: methoxyl, 9·78; $C_{16}H_{12}O_5$ requires 10·92%). The preparation of the 7-methyl ether of baicalein was described by Sastri and Seshadri.[3] Its properties were different from those of oroxylin-A, thus eliminating this possibility.

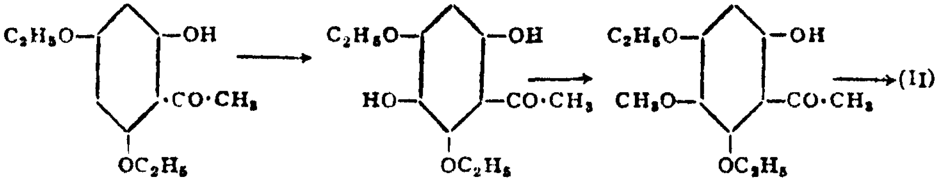
Since Shah, *et al.*,[1] were unsuccessful in their attempt to synthesise oroxylin-A, getting wogonin instead, we proposed to provide confirmation of its constitution by the synthesis of its diethyl ether according to the scheme adopted earlier in the case of patuletin which is the 6-methyl ether of quercetagetin.[4] An authentic sample of oroxylin-A was required for this purpose and as it was not available, it was prepared from the root bark of *Oroxylum indicum* obtained from Travancore. Using the method of the earlier workers it was easy to obtain the substance melting at 231–32° and free from baicalein. Though its methylation yielded baicalein trimethyl ether fairly readily, its ethylation product melted low and indefinitely, and had to be repeatedly recrystallised a number of times in order to raise the melting point to that of a synthetic sample of 6-methoxy-5 : 7-diethoxyflavone. A similar difficulty was noted in regard to the acetylation product which did not melt sharp (m.p. 131–35°). Methoxyl estimation gave low values. It appeared therefore that the original substance was still a mixture though rather sharp melting. Very similar results were obtained when stem bark samples procured from Travancore as well as from Calcutta were extracted adopting the same procedure. Attempts were then made to separate the mixture by the chromatographic method; they were unsuccessful. Eventually fractional crystallisation of the acetates from ethyl alcohol was found to be satisfactory. The least soluble fraction melted high and yielded pure chrysin acetate on further crystallisation. The middle fraction yielded on further crystallisation a sharp melting acetate (139–40°) which had the correct composition of the diacetate of oroxylin-A, this name being retained for the 6-methyl ether of baicalein. On deacetylation using acid or alkali it yielded a sharp melting uniform sample having the correct composition required for the 6-methyl ether of baicalein. But the melting point was 219–20°, considerably lower than that found for the mixture. Its correctness was confirmed in the following manner. From the methoxyl value of our sample melting at 231–2°, it could be estimated that it was roughly a mixture of 70 parts of oroxylin-A and 30 of chrysin. A mixture of this composition was made from pure entities and also another in the proportion of 60 : 40. The former melted at 233–4° and the latter at 236–7°. Though in these mixtures the major component was oroxylin-A and chrysin may be considered to be an impurity, the melting points were definitely higher than that of pure oroxylin-A.

The purified sample of oroxylin-A melting at 219–20° yielded a sharp melting acetate (139–40°) and a sharp melting diethyl ether readily. The latter was found to be identical with a synthetic sample of 6-methoxy-5 : 7-diethoxy flavone (II), thus providing definite confirmation of the proposed constitution of oroxylin-A.



(I) (II)

The synthesis started from phloroacetophenone which was first converted into the 4 : 6-diethyl ether (III) by partial ethylation in acetone solution using two moles of ethyl iodide and excess of anhydrous potassium carbonate (compare Row and Seshadri[4]). This compound was earlier prepared by Kostanecki[5] by the partial de-ethylation of phloroacetophenone-triethyl ether with anhydrous aluminium chloride. When oxidised with potassium persulphate in alkaline medium it yielded 2 : 5-dihydroxy-4 : 6-diethoxy acetophenone (IV) which was also characterised by the preparation of its dibenzoate. The constitution of this dihydroxy compound arrived at by close analogies was further supported by its properties. It was then subjected to partial methylation to form 2-hydroxy-5-methoxy-4 : 6-diethoxy-acetophenone.



(III) (IV) (V)

Later two methods were adopted. The above ketone was condensed with benzoic anhydride and sodium benzoate according to the method of Allan and Robinson. In order to decompose the 3-benzoyl derivative that was formed, boiling with aqueous sodium carbonate was employed. The product gave appreciable colour with alcoholic ferric chloride indicating that some de-ethylation had occurred in the 5-position during the above condensation. It was therefore finally ethylated to yield (II). As the second alternative the ketone (V) was converted into the flavone (II) according to the procedure of Baker and Venkataraman. The same compound melting at 115-16° was obtained by both ways and as already mentioned it was identical with O-diethyl-oroxylin-A.

From the results recorded above it could be concluded that the root as well as stem barks of *Oroxylum indicum* contain baicalein and chrysin along with oroxylin-A. Its correct melting point is 219–20° and its constitution as 6-O-methyl-baicalein is confirmed by the unambiguous synthesis of its diethyl ether.

EXPERIMENTAL

Extraction of the Root Bark of Oroxylum indicum

The powdered root bark (1·5 kg.) was extracted in the cold with acetone for 48 hours. The extract was tapped off and the extraction repeated twice again. The combined extracts were distilled to recover the solvent. The concentrate on allowing to stand for two days deposited a heavy yellow crystalline solid. It was filtered and washed with small amounts of cold acetone. Yield, 33·0 g. It sintered at 210° and melted at 222–4°.

The crude product (10 g.) was crystallised twice from alcohol when it was obtained as a bright yellow crystalline solid. It was powdered well in a mortar and ground up thoroughly with 10% aqueous sodium hydroxide (50 c.c.). The greenish blue mixture was transferred to a conical flask and treated with a further volume (200 c.c.) of aqueous alkali. After shaking thoroughly it was left overnight. The heavy greenish blue precipitate was filtered off and a clear yellowish brown filtrate obtained. It was acidified with hydrochloric acid and the pale yellow solid precipitate recovered by filtration. It was crystallised twice from alcohol when the product was obtained as yellow shining narrow rectangular plates melting at 231–2°. Yield, 6·0 g. (Found: CH_3O, 7·2; $C_{16}H_{12}O_5$ requires CH_3O, 10·9%).

Fractionation of Acetate

The purified, dry product (6 g.) was refluxed with acetic anhydride (30 c.c.) and fused sodium acetate (5 g.) for an hour and a half. The excess of acetic anhydride was then decomposed by adding the cold mixture to ice-water (200 c.c.). The precipitated acetyl derivative was filtered, washed with water and crystallised from alcohol. The acetyl derivative was thus obtained as colourless needles melting between 131–135°.

Fraction (i)—*Chrysin Acetate*

The crude acetyl derivative was dissolved in just sufficient amount of boiling alcohol and filtered. On cooling, the filtrate deposited colourless crystals (1·5 g.) which formed fraction (i) and melted at 180–4°. It was crystallised twice from alcohol when the compound was obtained as colourless wedge-shaped plates melting at 192–3°. The mixed melting point with an authentic sample of chrysin acetate was not depressed. When deacetylated with alcoholic hydrochloric acid, it yielded pale yellow prismatic needles melting at 275–6° identical with an authentic sample of chrysin.

Fraction (ii)—*Acetate of Oroxylin-A*

The filtrate from fraction (i) was concentrated to half its original volume and was left aside. After a few hours. the crystalline solid that separated was filtered and washed with cold acohol. This fraction (ii) melted at 137–38° and weighed 2·5 g. When recrystallised twice from alcohol, it came out in the form of colourless long rectangular plates and rods melting at 139–40°. There was no rise in the melting point after a further crystallisation. (Found: C, 64·8; H, 4·5; CH_3O, 8·7; $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3 and CH_3O, 8·4%).

Fraction (iii)

The mother liquor from fraction (ii) was further concentrated. Only a semi-solid mass could be recovered from it. On pressing it over a filter-paper, some solid was obtained, which melted indefinitely between 95 and 105°. Further fractionation of this solid did not yield fruitful results.

Oroxylin-A

The hydrolysis of the acetate from Fraction (ii) was effected by two methods: (*a*) acid hydrolysis and (*b*) alkali hydrolysis.

Acid hydrolysis.—The acetate (0·5 g.) was dissolved in alcohol (50 c.c.) and an equal volume of concentrated hydrochloric acid added; the mixture was refluxed for two hours. The alcohol was removed under reduced pressure when a solid product separated out. It was crystallised twice from alcohol when yellow elongated rectangular prisms were obtained melting at 219–20°. Further crystallisation did not improve the melting point.

Alkali hydrolysis.—The acetate (0·5 g.) was left overnight with 10% aqueous sodium hydroxide with occasional stirring. The solid which at first was insoluble, slowly went into solution. The clear reddish yellow solution was acidified next morning. The pale yellow solid, obtained thereby, was crystallised from alcohol. After two crystallisations, yellow elongated rectangular prisms were obtained melting at 219–20° which could not be improved further by crystallisation. The mixed melting point with 7-O-methyl-baicalein which also melts at this temperature was considerably depressed. (Found: C, 68·0; H, 4·4; CH_3O, 10·5; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2 and CH_3O, 10·9%). Pure oroxylin-A gave with alcoholic ferric chloride an olive brown colour and with alcoholic lead acetate a yellow precipitate which dissolved in excess of the reagent.

Another method of isolating chrysin from the mixture

The sample (1 g.) melting at 231–2° was dissolved in acetic anhydride (5 c.c.) and treated with hydriodic acid (d. 1·7; 10 c.c.). After refluxing for 1½ hours, the mixture was cooled, diluted with water and then saturated with sulphur dioxide. The bright yellow solid product was collected at the pump, washed with more sulphur dioxide-water and then transferred to aqueous sodium hydroxide (100 c.c., 10%). The mixture was shaken thoroughly and left overnight. It was then filtered through a fluted filter and the clear reddish yellow filtrate acidified with hydrochloric acid. A pale yellow solid separated out which after a crystallisation from alcohol was obtained as pale yellow prismatic needles melting at 275–6°. A second crystallisation from the same solvent did not improve the melting point. It did not also depress the melting point of an authentic sample of chrysin; yield, 0·3 g.

O-Diethyl-oroxylin-A

The sample of oroxylin-A (0·5 g.) melting at 219–20° was ethylated by refluxing with diethyl sulphate (2 c.c.) and anhydrous potassium carbonate (5 g.) in anhydrous acetone (50 c.c.). After 20 hours, the solvent was distilled off and the residue treated with water. The precipitated solid was filtered, washed with water and crystallised once from aqueous alcohol. The ethyl ether was readily obtained as colourless rectangular plates melting at 115–16° which was not depressed by a synthetic sample. Yield, 0·4 g. (Found: C, 70·3; H, 5·8; $C_{20}H_{20}O_5$ requires C, 70·6 and H, 5·9%).

2-*Hydroxy*-4 : 6-*diethoxy-acetophenone* (*III*)

Dry phloracetophenone (4·2 g.) was refluxed with ethyl iodide (4·3 c.c.) and anhydrous potassium carbonate (10 g.) in acetone solution (150 c.c.). After 12 hours, the solvent was distilled off and water added to the residue. The resulting solid was collected, washed with water and then taken up in ether. The ethereal solution was extracted thrice with 5% aqueous sodium hydroxide. The combined extracts were acidified with dilute hydrochloric acid when the ethyl ether was precipitated as a practically colourless crystalline solid. It was filtered, washed and crystallised from dilute alcohol. The ketone was now obtained as colourless thin, broad, rectangular plates melting at 86–87°. Its alcoholic solution developed an intense reddish brown colour with a drop of ferric chloride. Yield, 1 g.

2 : 5-*Dihydroxy*-4 : 6-*diethoxy-acetophenone* (*IV*)

To a continuously stirred solution of the above ketone (3·5 g.) in aqueous sodium hydroxide (60 c.c.; 10%) was added dropwise a solution of potassium persulphate (5 g.) in water (100 c.c.) during the course of 3 hours, the temperature being maintained at 15–20° throughout the addition. After 24 hours, the reddish brown solution was neutralised to litmus with hydrochloric acid and the unchanged ketone recovered by ether extraction. The liquid was then treated with sodium sulphite (5 g.) and concentrated hydrochloric acid (25 c.c.) and heated at 90° for half-an-hour. On cooling a brownish yellow crystalline solid was deposited. When crystalised from alcohol, 2:5-dihydroxy-4:6-diethoxy-acetophenone was obtained as yellow stout rhombic prisms and melted at 130–1°. It was easily soluble in hot alcohol and acetone but insoluble in petroleum-ether. In alcoholic solution, the substance gave a transient green colouration with a drop of ferric chloride and with excess of the reagent a deep reddish brown colour. It gave no precipitate with lead acetate in alocholic solution. (Found: C, 59·9; H, 6·9; $C_{12}H_{16}O_5$ requires C, 60·0; H, 6·7%). Yield, 0·8 g.

The dibenzoyl derivative was prepared by heating the dihydroxy ketone with benzoyl chloride and pyridine on the water-bath. The product was diluted with water, and the precipitated solid was filtered and crystallised from alcohol; m.p. 154–5°. (Found: C, 69·9; H, 5·5; $C_{26}H_{24}O_7$ requires C, 69·6 and H, 5·4%).

Partial methylation of the above ketone

The 2:5-dihydroxy compound (IV) (1·6 g.) was dissolved in dry acetone (75 c.c.) and treated with acid-free dimethyl sulphate (0·7 c.c.) and anhydrous potassium carbonate (3 g.). After refluxing for 12 hours, the potassium salts were filtered and washed well with warm acetone. After distilling off the acetone from the filtrate, the residue was taken up in ether and extracted thrice with 5% aqueous alkali. The extracts were acidified with hydrochloric acid. The product was taken up in ether and the ether solution dried over sodium sulphate. On removing the solvent a reddish-brown oil was obtained which did not solidify even on keeping in the refrigerator for 3 days. It was then treated with light petroleum (40–60°) when the unchanged dihydroxy compound along with some resinous impurity was left behind. The petroleum ether solution was carefully decanted and the solvent distilled off when the partial methyl ether was obtained as a bright yellow oil. Yield, 0·8 g. It dissolved in aqueous sodium hydroxide to give an yellow solution and its alcoholic solution developed a violet-brown colour with a drop of ferric chloride. It did not solidify on standing or cooling and could not be further purified. It was used directly for the next stage of synthesis.

6-*Methoxy*-5:7-*diethoxy flavone* (*II*): (*a*) *Allan-Robinson Method*

An intimate mixture of the above partial methyl ether (V) (2 g.), benzoic anhydride (12 g.) and sodium benzoate (4 g.) was heated between 170–80°, under reduced pressure for three hours. The cooled mass was then refluxed with alcoholic potash (10%; 75 c.c.) for 20 minutes and then after the removal, of the solvent by distillation under reduced pressure, dissolved in water and saturated with carbon dioxide. A dark brown solid separated out.

It was further boiled with aqueous alcoholic sodium carbonate (5%) for about two hours. After distillation of the alcohol and acidification the solid product was filtered and crystallised from alcohol using animal charcoal. It gave a green colouration with alcoholic ferric chloride indicating partial de-ethylation. So it was ethylated further using excess of ethyl sulphate and potassium carbonate in anhydrous acetone medium. After refluxing for 12 hours the solvent was distilled off and water added to the residue. A brownish white solid separated out. It was crystallised from aqueous alcohol when 6-methoxy-5:7-diethoxy flavone was obtained as colourless narrow rectangular plates melting at 115–6°. It gave no colour with ferric chloride in alcoholic solution and did not dissolve in aqueous akali. (Found: C, 70·5; H, 5·8; $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

(b) Baker and Venkataraman Method

Benzoylation.—The partially methylated ketone (V) (1·5 g.) was benzoylated by heating with benzoyl chloride (1 c.c.) and pyridine (8 c.c.) on the water-bath for 30 minutes. The benzoyl derivative separated out as a pale brown oil when the mixture was diluted with ice-cold dilute hydrochloric acid. It was taken up in ether and washed with 3% aqueous sodium hydroxide in order to remove any unchanged ketone and benzoic acid and then with very dilute hydrochloric acid and water. After drying over calcium chloride, the ether was removed when the benzoyl derivative was obtained as a practically colourless semi-solid mass. Yield, 1·5 g. It was insoluble in aqueous alkali and gave no colour with alcoholic ferric chloride. Various attempts at crystallisation from alcohol, alcohol-benzene mixture, and petroleum ether-acetone mixture failed. It was, therefore, directly employed for conversion into the dibenzoyl methane.

Transformation.—The foregoing benzoyl derivative was heated with finely powdered sodamide (10 g.) in dry toluene medium on the water-bath for four hours with frequent shaking. The solid sodium derivative was then filtered, washed well with warm benzene and after drying added in small quantities to ice-water. After the exces of sodamide had completely decomposed, the bright yellow solution was saturated with carbon dioxide. The dibenzoyl methane was obtained as an orange yellow oil. It was taken up in ether and dried over sodium sulphate. When the solvent was removed again a bright yellow oil was obtained. It did not crystallise on standing or cooling. It easily dissolved in aqueous alkali and gave a deep reddish brown colour with a drop of ferric chloride. Yield, 0·9 g.

Ring closure.—The above dibenzoyl methane (0·7 g.) was treated with glacial acetic acid (8 c.c.) and anhydrous sodium acetate (2 g.) and the mixture gently refluxed for 4 hours. After dilution with water, it was extracted with ether, the ether layer shaken with sodium hydroxide to remove acetic acid and any phenolic material. After washing with very dilute hydrochloric acid and water, the ether solution was dried over calcium chloride and the solvent removed. The flavone was obtained as a colourless oil which solidified on keeping in the refrigerator for 12 hours. It crystallised from petroleum-ether-acetone mixture as narrow rectangular plates and flat needles melting at 115–116°. It was insoluble in aqueous alkali and gave no colour with alcoholic ferric chloride. It agreed in every respect with the sample obtained by the Allan-Robinson method.

SUMMARY

The experiments described in this paper show that a pure sample of oroxylin-A melts at 219–20° (acetate, 139–40°), that the substance melting at 231–32° is a mixture of it with chrysin and that this mixture could be separated by fractionation of the acetates. The constitution of oroxylin-A as the 6-methyl ether of baicalein is confirmed by ethylating it to the diethyl ether and showing that the product is identical with a synthetic sample of 6-methoxy-5: 7-diethoxy flavone. The details of the synthesis are given.

Our thanks are due to Miss A. Kameswaramma, M.Sc., for verifying some of the results.

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A NEW EFFECT OF HYDROGEN BOND FORMATION (CHELATION)

Part II. Constitution of Despedicellin, Dihydropedicinin and Isopedicin

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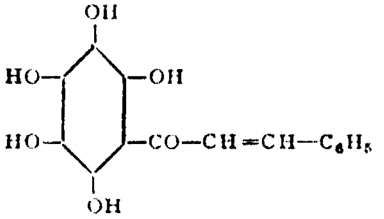
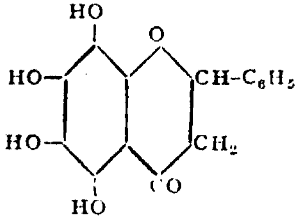
Despedicellin was obtained by the action of hydriodic acid on pedicellin, pedicin and pedicinin.[1] It was given the pentahydroxy chalkone structure (I). A substance of this constitution would normally be expected to have a bright red colour but despedicellin is only a pale straw yellow crystalline substance. This property would suggest that it is a flavanone (II) which should also be expected in accordance with the observations recorded in Part I of this series[2] and the explanations offered. Owing to the formation of hydrogen bonds, whenever there are two hydroxyl groups in the 2:6-positions of a chalkone it should be expected to undergo ready conversion into the flavanone which has a high degree of stability.



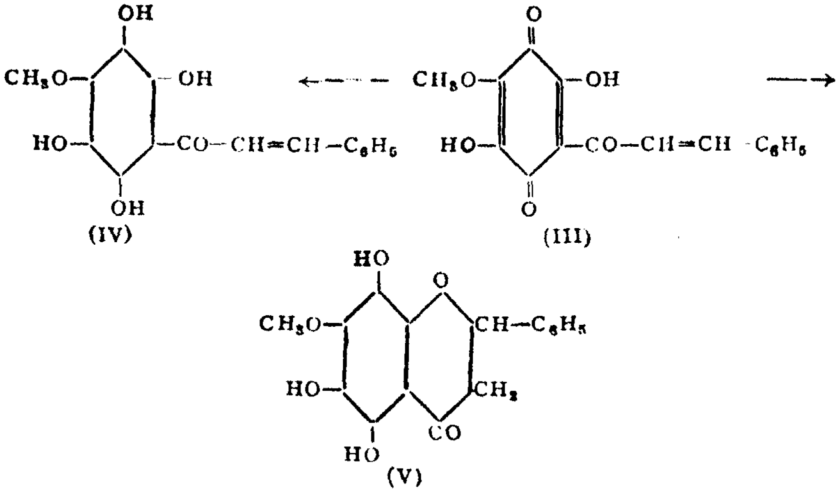
(I)



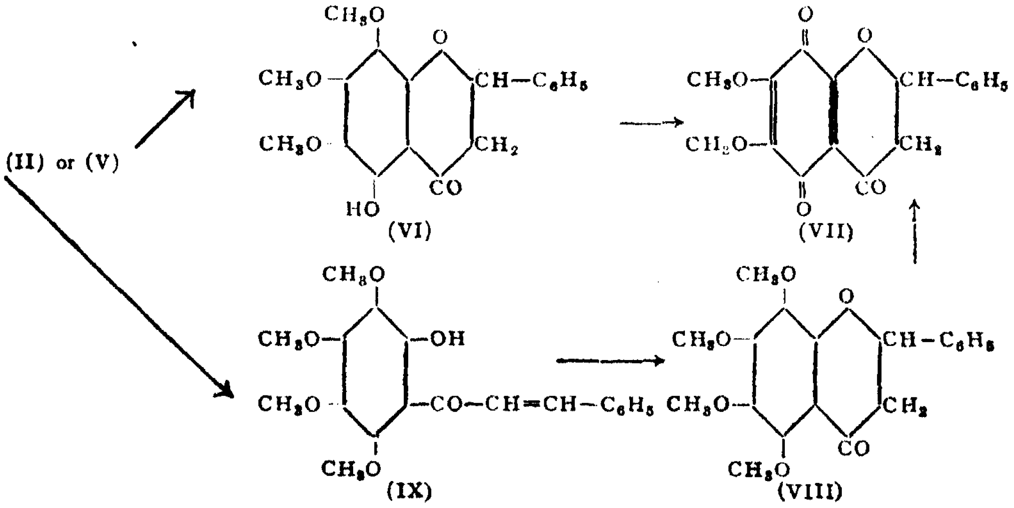
(II)

The position seems to be quite similar in the case of dihydropedicinin obtained by the reduction of pedicinin using stannous chloride and hydrochloric acid.[3] Since the constitution of pedicinin has been conclusively shown to be that of a hydroxy-quino-chalkone (III),[4] it follows that the reduction product should be either a tetrahydroxy chalkone (IV) or the corresponding flavanone (V). The lack of prominent colour even in this case would indicate that dihydropedicinin is also a flavanone (V).

In the course of the work presented in this paper a detailed study of the properties of these compounds has been made in order to get more precise information regarding their constitution. Methylation in stages using dimethyl sulphate and potassium carbonate as was described in Part I[2] in connection with naringin and naringenin was first attempted. Using five molecular proportions or excess of dimethyl sulphate despedicellin could now be readily and completely methylated to pedicellin though reports of


(IV) (III) (V)

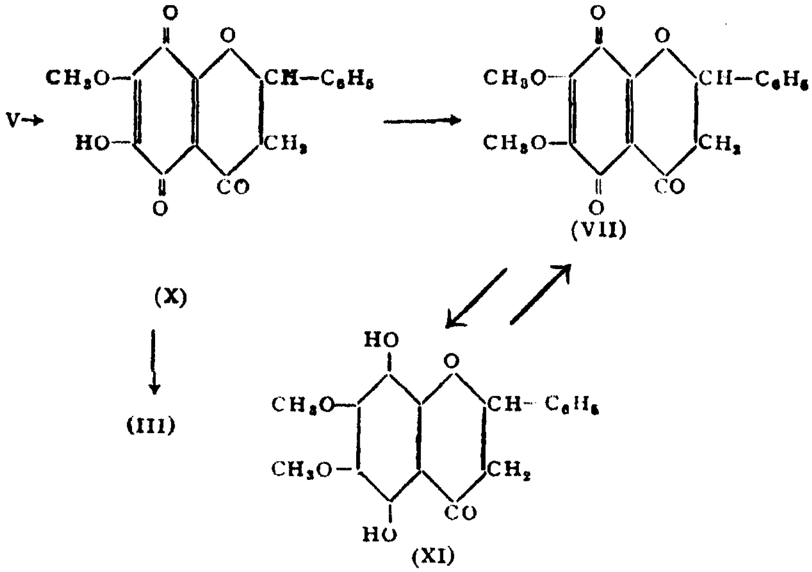
unsuccessful attempts were made by earlier authors.[1] But partial methylation with three molecular proportions of this reagent to yield the 5-hydroxy flavanone derivative has not been quite successful owing to its low melting point and high solubility in organic solvents. Hence the use of diazomethane has been examined next. It is well established that this reagent does not attack the 5-hyndroxyl group of flavanones even when used in excess. By its action on despedicellin or dihydropedicinin is obtained the same compound melting at 99–100° and having only a very pale yellow colour. It has three methoxyl groups in the molecule and gives a prominent green colour with ferric chloride. All these properties agree with the structure of 6:7:8-trimethoxy-5-hydroxy flavanone (VI). If the above compounds were chalkones, a tetramethyl ether would have resulted.


(VI) (VII) (IX) (VIII)

Further the trimethyl ether (VI) undergoes oxidation with nitric acid to form a quinone (VII) which is identical with the substance obtained by the oxidative demethylation of 5:6:7:8-tetramethoxy flavanone (VIII). This last mentioned compound (VIII) is prepared by the methylation of despedicellin (II) using four molecular proportions of dimethyl sulphate and cyclising the resulting tetramethoxy chalkone (IX) by means of alcoholic hydrochloric acid.

The formation of the chalkone derivative (IX) from despedicellin (II) is in line with similar observations made in the case of naringin and naringenin,[3] where also the flavanone ring was found to open out under the conditions of this methylation as soon as the 5-hydroxyl group gets methylated. The tetramethoxy chalkone (IX) is an orange coloured liquid giving a reddish brown colour with alcoholic ferric chloride. The tetramethoxy flavanone (VIII) obtained from it is colourless and does not exhibit any colour with ferric chloride but when treated with alkali it readily gets converted into the chalkone (IX). It is interesting that this flavanone (VIII) undergoes simple oxidative demethylation giving 6:7-dimethoxy-quinoflavanone (VII) as the main product. In this respect the tetramethoxy flavanone resembles the corresponding members of the flavone series (*e.g.*, calycopterin dimethyl ether) which also give rise to methoxy quinones.[5] But in the reaction with the flavanone a small quantity of pedicinin is also obtained as a result of the reaction going further involving opening of the ring and demethylation of another methoxyl group. The important point to be noted is that the quinone obtained from the tetramethoxy flavanone (VIII) is different from pedicinin and methyl pedicinin and has two methoxyl groups and thus is undoubtedly a flavanone derivative. The identity of this compound with the one obtained from the trimethyl ether (VI) resulting from despedicellin and dihydropedicinin should be taken as an additional proof of the flavanone nature of this partial methylation product and consequently of the original compounds, despedicellin and dihydropedicinin.

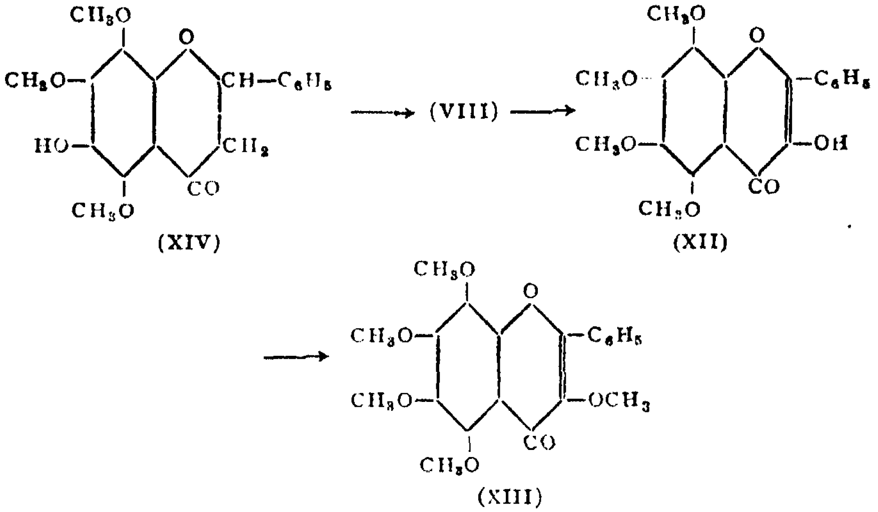
The action of benzoquinone on these two compounds has been next investigated. In agreement with the behaviour of similar compounds in the flavone series,[6] despedicellin does not form any sparingly soluble quinone. On the other hand, dihydropedicinin readily yields the corresponding quinone (X), with this reagent. It is a deep orange coloured crystalline solid which is quite different from pedicinin but is isomeric. It can be converted into the latter by treatment with alkali and it is therefore named allopedicinin since the name isopedicinin has earlier been employed in another connection.[2] It could also be readily methylated with diazomethane to yield a monomethyl derivative, 6:7-dimethoxy-quino-flavanone (VII) which has been already mentioned. This last mentioned quinone can further be reduced by means of sulphurous acid to the corresponding quinol (XI) and the reverse oxidation can be effected using benzoquinone. These reactions are again explicable only on the flavonone structure for these compounds.



Yet another unequivocal evidence is provided by the determination of active hydrogen atoms using magnesium methyl iodide. Despedicellin gives evidence for the presence of only four hydroxyl groups and dihydropedicinin for only three. The chalkone constitution would require one more active hydrogen atom for each of them.

Since support for the flavanone structure for despedicellin and dihydropedicinin rests upon the constitution of the tetramethoxy compound (VIII) it has been felt necessary to confirm its structure as a flavanone. This has been done by converting it into the corresponding flavonol (XII) by means of isoamyl nitrite and hydrochloric acid. The 3-hydroxy compound (XII) thus obtained on methylation yields the already known pentamethyl ether (XIII) of 6:8-dihydroxy-galangin.[7]

In an earlier publication[4] it was concluded that isopedicin is 6-hydroxy-5:7:8-trimethoxy flavanone (XIV) and in support of this constitution it was pointed out that it could be obtained from pedicin by the ordinary chalkone-flavanone conversion and could be changed into pedicin easily by treatment with dilute alkali. In confirmation of this it is now shown



that it could be readily methylated with diazomethane and the product is 5 : 6 : 7 : 8-tetramethoxy flavanone (VIII).

Experimental

Despedicellin (II)

The following is a more convenient method of preparation than that described by Sharma and Siddiqui.[1] Pedicellin (5 g.) was dissolved in acetic anhydride (10 c.c.), hydriodic acid (20 c.c., d. 1·7) added and the mixture boiled for 1½ hours. During the later stages of the reaction a considerable amount of a crystalline solid separated out. The mixture was cooled, diluted with water and the free iodine removed by adding sodium sulphite. It was then heated to boiling, cooled and the pale yellow glistening crystals filtered. Yield 3·3 g. When recrystallised from hot alcohol, despedicellin separated out as pale yellow glistening micaceous plates melting at 255–56°. (Found: C, 55·4; H, 5·2; $C_{15}H_{12}O_6$, $2H_2O$ requires C, 55·6; H, 4·9%.)

It was sparingly soluble in alcohol and ether. When one drop of aqueous ferric chloride was added to an alcoholic solution of the substance a dark greenish blue colour was produced; the solution soon changed almost colourless and slowly developed a pale brown violet colour. The changes were markedly accelerated by the addition of another drop of the reagent. It was sparingly soluble in aqueous sodium bicarbonate. In 5% aqueous sodium carbonate it dissolved to a greenish yellow solution which changed to orange yellow. The colour reaction with caustic alkali seems to vary with the strength of the reagent and other conditions of observation. In 5% sodium hydroxide, the initial yellow colour changed on shaking to greenish yellow and olive green which became brown red and orange and later faded slowly. When treated with *p*-benzoquinone in alcoholic solution an intense red colour was obtained which slowly faded to pale brown in the course of a few minutes. With lead acetate in alcoholic solution was formed a deep orange red precipitate which soon changed to dirty brown and later bluish green. The subsance was stable when boiled in alcoholic solution from which it can be best crystallised.

Complete methylation of despedicellin: Pedicellin

A solution of despedicellin (1 g.) in anhydrous acetone (50 c.c.) was treated with dimethyl sulphate (3 c.c.) and potassium carbonate (8 g.). After refluxing the mixture for 10 hours, the solvent was completely distilled off and the residue treated with water (50 c.c.). The mixture was cooled in ice water for 30 minutes, the undissolved white solid was filtered, washed and dried. Crystallisation from ligroin gave colourless rectangular prisms melting at 97–98°. It was identical with pedicellin.

Partial methylation of despedicellin

(i) *With diazomethane*: 5-*Hydroxy*-6 : 7 : 8-*trimethoxy flavanone* (*VI*).—A solution of despedicellin (0·8 g.) in a mixture of absolute alcohol (10 c.c.) and ether (20 c.c.) was treated with an ethereal solution of diazomethane prepared from nitrosomethyl urea (2·8 g.). The methylating agent was added in small lots with cooling in ice during 10 minutes. The initial brown colour of the solution changed to pale yellow and the reaction mixture was then kept in an ice-chest for 2 days, the container being closed with a one-holed cork carrying a capillary tube to allow for the escape of gases evolved. The solvents were completely distilled off and the residue taken up in hot ligroin. On concentrating this solution and cooling in ice-water for a few hours the methyl ether crystallised. It was purified by recrystallisation from ligroin from which it separated out in the form of pale yellow prismatic needles melting at 99–100° (Found: C, 65·7; H, 5·8, OCH_3, 28·7; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5; methoxyl for 3 OCH_3, 28·2%). It was readily soluble in most organic solvents and sparingly in cold ligroin. In alcoholic solution it gave a stable intense green colour with ferric chloride. It was not soluble in cold aqueous sodium hydroxide but dissolved on heating to give deep yellowish brown solution.

(ii) ***With dimethyl sulphate***: *2-hydroxy-3 : 4 : 5 : 6-tetramethoxy chalkone* (*IX*).—A mixture of despedicellin (3 g.), dimethyl sulphate (4 c.c.), acetone (50 c.c.) and anhydrous potassium carbonate (10 g.) was refluxed for 8 hours. The solvent was distilled off and the brown residue treated with water (100 c.c.).

The mixture was extracted twice with ether and the ether extract marked (A) was shaken repeatedly with 5% sodium hydroxide. On acidifying the combined alkaline extracts with concentrated hydrochloric acid an orange yellow liquid was formed. It was extracted with ether, the ether extract dried over anhydrous sodium sulphate and distilled; 2-hydroxy-3:4:5:6-tetramethoxy chalkone separated out as a thick orange yellow oil. It did not crystallise even on keeping for a long time in the ice-chest. It was sparingly soluble in aqueous sodium hydroxide and in alcoholic solution it gave a deep reddish brown colour with ferric chloride. Yield, 1·5 g. Without further purification it was directly used for flavanone ring closure.

The alkali treated ether extract (A) on evaporation left a brown viscous semi-solid. It was digested with hot aqueous sodium hydroxide and cooled. The light brown solid was filtered from the alkaline solution and crystallised from ligroin. It formed colourless rectangular prisms melting at 97–98° and was identical with pedicellin. Yield 1 g.

Attempts were made to prepare this tetramethoxy-chalkone by the partial demethylation of pedicellin using hydrobromic acid in glacial acetic acid solution. But they were not successful. From the mixture that was formed despedicellin alone could be isolated pure.

5:6:7:8-*Tetramethoxy flavanone* (*VIII*)

A solution of 2-hydroxy-3:4:5:6-tetramethoxy chalkone prepared as described above (1 g.) was dissolved in alcohol (25 c.c.) and the solution treated with concentrated hydrochloric acid (2 c.c.) and water (10 c.c.). The mixture was gently refluxed for 24 hours and at the end of this period the alcohol was distilled off as far as possible under reduced pressure. The residue was poured into water (50 c.c.) and the mixture extracted twice with ether. The ether extract was washed with 5% aqueous sodium hydroxide twice to remove the unchanged chalkone. The extract was finally washed with water, dried over anhydrous sodium sulphate and distilled. The very pale yellow liquid product that was left behind soon became crystalline. It was recrystallised from ligroin from which it separated out in the form of colourless broad rectangular plates melting at 78–79° (Found: C, 66·4; H, 6·2; OCH_3, 35·5; $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·8; 4 OCH_3, 36·0%).

It was easily soluble in most organic solvents and sparingly in ligroin. It did not give any colour with ferric chloride in alcoholic solution. It did not dissolve in cold aqueous sodium hydroxide but on heating dissolved to give a bright yellow solution. The recovered chalkone could be used again for the conversion into the flavanone.

(ii) A solution of isopedicin[4] (made from pedicin) (0·5 g.) in ether (25 c.c.) was treated with an ethereal solution of diazomethane from nitrosomethyl urea (0·5 g.). The reaction mixture was kept in the ice-chest for two days and the solvent completely distilled off. The residual pale yellow liquid was taken up in ether and shaken with dilute aqueous sodium hydroxide which removed the unchanged isopedicin. The ether solution was washed with water, dried over anhydrous sodium sulphate and distilled. The tetramethoxy flavanone left behind soon crystallised. On recrystallisation from ligroin it separated out in the form of colourless broad rectangular plates melting at 78–79° alone or in admixture with the 5 : 6 : 7 : 8-tetramethoxy flavanone prepared from the corresponding chalkone.

3-*Hydroxy*-5 : 6 : 7 : 8-*tetramethoxy flavone* (*XII*)

A solution 5 : 6 : 7 : 8-tetramethoxy flavanone (0·5 g.) in alcohol (20 c.c.) was heated to boiling and the hot solution was treated alternately with freshly prepared amyl nitrite (6 c.c.) and concentrated hydrochloric acid (20 c.c., d. 1·19) during the course of half an hour while keeping the mixture gently boiling. The deep red reaction mixture was set aside for two hours and poured into water (200 c.c.). After cooling in the ice-chest overnight the yellow semi-solid mass was separated by filtration, washed with water and taken up in ether. The ether solution was dried over anhydrous sodium sulphate and distilled. The yellow liquid left behind crystallised on keeping in contact with a little ether. On recrystallisation from a mixture of ether and light petroleum it separated out as glistening yellow rectangular plates melting at 131–32° (Found: C, 63·4; H, 5·5; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%). It was sparingly soluble in aqueous sodium hydroxide and in alcoholic solution it gave a violet brown colour with ferric chloride. Yield, 0·1 g. On acetylation it yielded the acetyl derivative which crystallised from a mixture of benzene and ligroin as colourless rectangular plates melting at 122–23°.

3 : 5 : 6 : 7 : 8-*Pentamethoxy flavone* (*XIII*)

3-Hydroxy-5 : 6 : 7 : 8-tetramethoxy flavone (0·1 g.) was methylated in anhydrous acetone (25 c.c.) by refluxing with dimethyl sulphate (0·3 c.c.) and potassium carbonate (2 g.) for 10 hours. The potassium salts were filtered off, washed with hot acetone and the combined acetone filtrate distilled. The residue crystallised soon on adding a few drops of water. It was recrystallised from a mixture of ether and light petroleum when it separated out as colourless rectangular plates melting at 88–89°. It was identical with 3 : 5 : 6 : 7 : 8-pentamethoxy flavone described by Seshadri and

Venkateswarlu[7] and the mixed melting point was undepressed. The sample prepared by the older method when crystallised as given above melts at this higher temperature instead of at 80–82°.

Dehydrogenation of dihydropedicinin (V) to allo-pedicinin (X)

A solution of dihydropedicinin[8] (0·5 g.) in alcohol (5 c.c.) was diluted with ether (50 c.c.) and treated with pure *p*-benzoquinone (0·5 g.). The pale yellow colour immediately changed to deep red and in a few minutes orange red shining crystals began to separate out. After keeping the reaction mixture for 3 hours at the laboratory temperature, the crystalline solid was filtered and washed with small quantities of ether. The filtrate cone tained quinhydrone and the unchanged benzoquinone mostly. The quinonon the filter (Yield, 0·35 g.) was recrystallised twice from benzene from which it separated out in the form of glistening orange red feathery rhombic plates melting at 183–84° (Found: C, 64·0; H, 4·3; $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0%). It was sparingly soluble in ether but dissolved more easily in benzene and ethyl acetate. In distilled water and alcohol it dissolved to give a stable permanganate colour. With ferric chloride in alcoholic solution the purple colour changed to brown and with lead acetate an immediate flesh-coloured precipitate was formed.

Conversion of allo-pedicinin (X) into pedicinin (III)

Allo-pedicinin prepared as described above (0·1 g.) was treated with 10% aqueous sodium hydroxide (5 c.c.). The solid readily dissolved to a purple solution which immediately changed to red. After two minutes the solution was acidified with concentrated hydrochloric acid. The orange red crystals that separated out in a few minutes were collected by filtration, washed well with water and dried. Crystallisation from benzene gave deep red rectangular plates melting at 202–3°, alone or in admixture with an authentic sample of pedicinin.

Methylation of allo-pedicinin (X) to 6:7-dimethoxy-5:8-quino-flavanone (VII)

A solution of allopedicinin (0·3 g.) in alcohol (10 c.c.) was treated with an ethereal solution of diazomethane prepared from nitrosomethyl urea (0·6 g.), added in small portions while cooling in ice. During the later stages of the addition an orange coloured crystalline solid separated out. The mixture was left in the ice-chest overnight. The dimethoxy quinone that separated out was filtered off and washed well with ether. The filtrate on evaporation did not give any crystalline substance. The quinone was purified by recrystallisation from ethyl acetate when it separated as glistening orange rectangular plates melting at 189–90° (Found: C, 65·4; H, 4·8;

$C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%). Yield, 0·26 g. Unlike allopedicinin, the dimethoxy quinone was not soluble in water and it did not also give any colour with alcoholic ferric chloride. It slowly dissolved in aqueous sodium hydroxide to an orange red solution.

5:8-*Dihydroxy*-6:7-*dimethoxy flavanone* (*XI*)

A solution of 6:7-dimethoxy-5:8-quino-flavanone (VII) described above (0·1 g.) in glacial acetic acid (2 c.c.) was treated with sodium sulphite (0·5 g.). On heating for a few seconds the red colour of the solution changed to brownish yellow. The solution was diluted after two minutes with water (50 c.c.) and the yellow solid that separated out was collected, filtered, washed and dried. Crystallisation from ethyl acetate gave glistening yellow rectangular prisms melting at 212–14° (Found: C, 65·0; H, 5·4; $C_{17}H_{16}O_6$ requires C, 64·6; H, 5·1%). In aqueous sodium hydroxide it readily dissolved to a deep orange red solution. With ferric chloride in alcoholic solution it gave a brown colour.

Partial methylation of dihydropedicinin (*V*) *to* 5-*hydroxy*-6:7:8-*trimethoxy flavanone* (*VI*)

Dihydropedicinin (0·4 g.) was dissolved in a mixture of alcohol (10 c.c.) and ether (20 c.c.) and the solution treated with an ether solution of diazomethane made from nitrosomethyl urea (1·2 g.). The methylation was carried out just as in the case of despedicellin. The product was taken up in ether and dried over anhydrous sodium sulphate. On evaporating the ether a pale yellow liquid was obtained which crystallised slowly on keeping in the ice-chest for some time. It was recrystallised from ligroin when it separated out in the form of very pale yellow prismatic needles melting at 99–100°. Mixed melting point with 5-hydroxy-6:7:8-trimethoxy flavanone prepared from despedicellin using diazomethane was not depressed. It was sparingly soluble in aqueous sodium hydroxide and gave an intense green colour with ferric chloride in alcoholic solution. Yield, 0·15 g.

6:7-*dimethoxy*-5:8-*quino-flavanone* (*VII*)

(*a*) *From* 5:6:7:8-*tetramethoxy-flavanone* (*VIII*)

A solution of 5:6:7:8-tetramethoxy flavanone (0·1 g.) in anhydrous ether (10 c.c.) was treated with fuming nitric acid (0·5 c.c.). The acid had to be added cautiously drop by drop while cooling the mixture in ice-water as otherwise a violent reaction resulted. On keeping stoppered for 15 minutes, the reaction mixture deposited orange red crystals of the quinone. It was filtered off and washed well with ether. The solid was macerated with

5% sodium carbonate solution for a few minutes, filtered, washed with water and recrystallised from ethyl acetate. It formed orange rectangular plates melting at 189–90° alone or in admixture with 6:7-dimethoxy-5:8-quino flavanone prepared by the methylation of allopedicinin.

(*b*) *From 5-hydroxy-6:7:8-trimethoxy flavanone* (*VI*)—

The above flavanone (0·1 g.) in anhydrous ether (5 c.c.) was treated with fuming nitric acid (0·2 c.c.). The product was worked up just as in the previous experiment. On crystallisation from ethyl acetate it was obtained as orange rectangular plates melting at 188–90° alone or in admixture with the sample obtained as above.

Estimation of active hydrogen

Methyl magnesium iodide was prepared in isoamyl ether solution (100 c.c.) using magnesium (6 g.) and methyl iodide (25 g.). Despedicellin and dihydropedicinin were dried in an air oven at 110–20° for 2 hours and about 0·5 g. of each was weighed out accurately and dissolved in pure anhydrous anisole (12 c.c.). The volume of methane generated by the addition of 5 c.c. of the above reagent was measured using a gas burette. (Found: Number of hydroxyl groups in despedicellin 4·12 and in dihydropedicinin 3·03. Required for the flavanone structure 4·00 and 3·00 and for the chalkone structure 5·00 and 4·00 hydroxyl groups for despedicellin and dihydropedicinin respectively.)

SUMMARY

Though despedicellin and dihydropedicinin are prepared from chalkones and were earlier given the chalkone constitution, their properties indicate that they are flavanones. This constitution is also in accordance with the recent discovery of the new effect of hydrogen bonds on the stability of flavanones. It is confirmed by the following experiments. (1) The two compounds undergo partial methylation with diazomethane yielding 5-hydroxy-6:7:8-trimethoxy-flavanone which forms with nitric acid 6:7-dimethoxy-quinoflavanone identical with the sample obtained from 5:6:7:8-tetramethoxy flavanone. (2) Dihydropedicinin undergoes oxidation with *p*-benzoquinone to form allopedicinin which is different from pedicinin. Methylation of this with diazomethane yields 6:7-dimethoxy-quinoflavanone. (3) The estimation of active hydrogen atoms agrees with the flavanone and not chalkone structure for these two compounds. That isopedicin is also a flavanone is confirmed by its methylation with diazomethane to 5:6:7:8-tetramethoxy flavanone. The constitution of the

important reference compound, tetramethoxy flavanone is established by its conversion into the corresponding flavonol.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XVI. A New Synthesis of Myricetin

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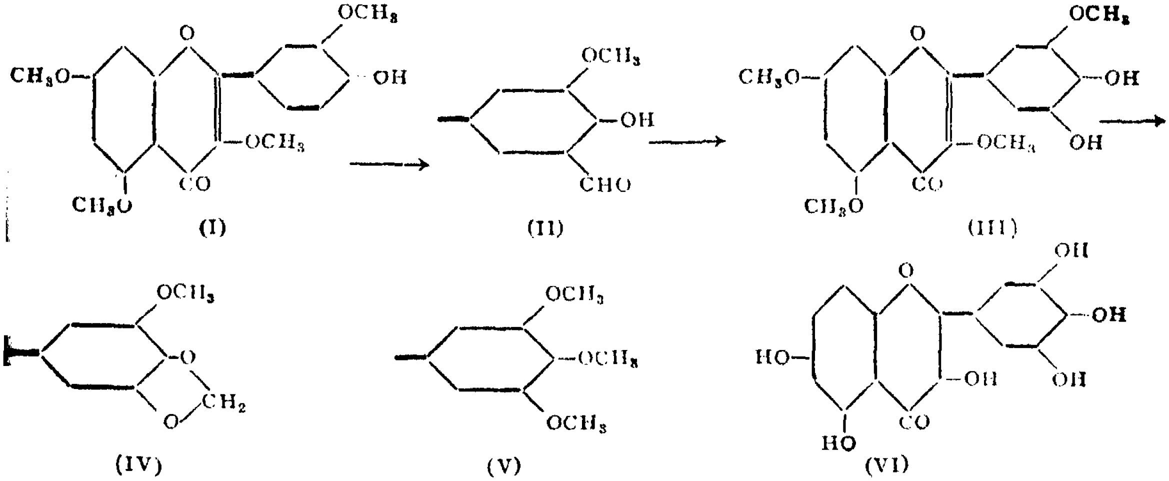
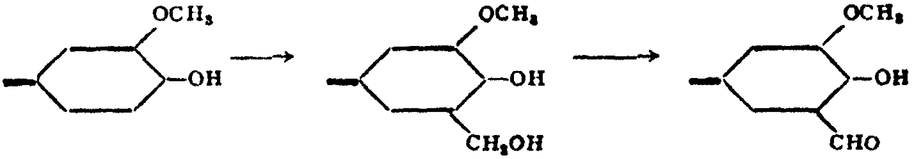
In Part XV[1] it was pointed out that ortho-oxidation in the side phenyl nucleus of flavones does not take place to any appreciable extent with alkaline persulphate and in fact this method of ortho-oxidation is unsatisfactory even in the case of simpler benzene derivatives. The conclusion was therefore drawn that an alternative method of oxidation should be available for this purpose. Persulphate as a reagent has been shown to be very similar to hydrogen peroxide[2] and its action may be considered to be a single stage oxidation process introducing directly a hydroxyl group in a reactive nuclear position. It is quite satisfactory for para oxidations and probably most para oxidations in nature take place by this direct process. For the majority of ortho-oxidations, however, this is unsuitable. They appear to proceed by a multi-stage process involving (1) introduction of an aldehyde group and (2) its replacement by a hydroxyl group. Hexamine and hydrogen peroxide used in the exploratory experiments described in Part XV seem to represent phytochemical reagent closely; this point will be discussed in detail later.

In the exploratory experiments on ortho-oxidation, as the most favourable example, the conversion of 3-methoxy-7-hydroxy flavone into 3-methoxy-7:8-dihydroxy flavone was studied. The results were highly successful and the yields quite good, being about 60% as against a maximum of 20% in the persulphate method. As the most appropriate example from the point of view of biogenesis, the synthesis of myricetin from a quercetin derivative has now been attempted. Quercetin-3:5:7:3′-tetramethylether (I) required for this purpose was described earlier as a stage in the synthesis of rhamnazin.[3] In the course of repetitions of its preparation a colourless by-product insoluble in alkali could be isolated. It is identified as galangin trimethyl ether. Its formation seems to be connected with the behaviour of the benzoyloxy groups in the reagents. In this connection may be mentioned the earlier observation of Allan and Robinson[4] that by heating ω-methoxy-phloroacetophenone with *o*-acetoxybenzoic anhydride and sodium *o*-acetoxybenzoate, the acetoxy groups alone functioned and that the product was 3-methoxy-5 : 7-dihydroxy-2-methylchromone. In the present case such reaction seems to proceed only to a minor extent. The quercetin tetramethyl ether reacts with hexamine readily and yields the corresponding 5′-aldehyde (II) which exhibits the characteristic reactions of an ortho-hydroxy aldehyde. Its oxidation with alkaline hydrogen peroxide produces myricetin tetramethyl ether (III) in very good yields. Like other catechols it gives characteristic colour reactions and reacts with methylene sulphate to form a methylene-dioxy compound (IV) analogous to kanugin. This product may be called 5-methoxy-kanugin; its constitution is definitely confirmed by its synthesis from ω : 4 : 6-trimethoxy-2-hydroxy acetophenone and the sodium salt and anhydride of myristicic acid. When, on the other hand, the catechol is methylated myricetin hexamethyl ether (V) and when demethylated myricetin (VI) itself are obtained.



Besides the experimental verification of the multi-stage theory of ortho-oxidation given above, closely related examples have also been examined successfully and they will be reported as early as possible. It may be useful to discuss here the choice of the reagents and their appropriateness for the theory of biogenesis. Since hexamine could be considered to be a convenient form of formaldehyde, then this aldehyde and hydrogen peroxide are the reagents involved in this type of oxidation and their availability in phytochemical processes can be granted. In regard to the action of formaldehyde it was suggested earlier in connection with the biogenesis of Lichen Acids,[5] that it is responsible for the introduction of the carbinol (CH_2OH), aldehyde (CHO) and related groups in certain active nuclear positions. The first would represent the earliest stage and as well known laboratory analogies could be mentioned the condensation of formalin with phenol, guaiacol, *p* and *o*-cresols,[6] and with *m*-hydroxy benzoic acid[7] yielding the corresponding benzyl alcohols or their derivatives. The next stage, *i.e.*, conversion of the carbinol into aldehyde can also be brought about by formaldehyde. In the laboratory synthesis with hexamine such an oxidation is evidently involved. A process somewhat analogous to the Meerwein-Pondorff reaction could be suggested for the conversion of alcohol (VIII) into aldehyde (IX) by means of formaldehyde though the possibility of other oxidising agents available in the plant taking part in this oxidation also exists.



(VII) (VIII) (IX)

Regarding phytochemical nuclear oxidation the position could now be stated as follows. The single stage process is quite satisfactory for the para; though it may not be precluded for the ortho it is inefficient. The multistage process on the other hand works very well for ortho-oxidation and it seems to be equally available for para oxidation.

EXPERIMENTAL

Condensation of ω:4:6-trimethoxy-2-hydroxy-acetophenone with the anhydride and potassium salt of benzoyl vanillic acid

An intimate mixture of ω:4:6-trimethoxy-2-hydroxy-acetophenone (2 g.), benzoyl vanillic anhydride (8 g.) and potassium benzoyl vanillate (3 g.) was heated under vacuo for 3 hours at 180°. The product was finely powdered and refluxed with 10% alcoholic potash (80 c.c.) for 30 minutes. The solvent was distilled off, the residue treated with water and the solution filtered from an insoluble yellowish grey soild (A). The filtrate on saturation with carbon dioxide gave quercetin 3:5:7:3′-tetramethyl ether (I) (1·6 g.) melting at 200–1°.[8] The solid marked (A) was crystallised from alcohol when it separated out as colourless rectangular prisms melting at 197–8°. It was insoluble in aqueous alkali and did not give any colour with ferric chloride. Mixed melting point with an authentic sample of galangin trimethyl ether was not depressed. Yield 0·4 g.

O-3:5:7:3′-Tetramethylquercetin-5′-aldehyde (II)

A solution of the tetramethyl quercetin (0·5 g.) in glacial acetic acid (6 c.c.) was treated with hexamine (2 g.). The clear pale yellow solution was kept in a boiling water-bath for 6 hours. At the end the deep yellowish brown solution was treated with a boiling mixture of concentrated hydrochloric acid (3 c.c.) and water (3 c.c.) and heated for 5 minutes. After adding more water (10 c.c.) it was left overnight whereby a greyish yellow solid crystallised out. Yield 0·25 g. It was purified by recrystallisation from a mixture of absolute alcohol and ethyl acetate when it appeared as yellow stout rectangular prisms melting at 217–18°. (Found: C, 62·2; H, 4·8; $C_{20}H_{18}O_8$ requires C, 62·2; H, 4·7%.) It was sparingly soluble in benzene, ether and ethyl acetate but more easily in alcohol and acetone. Very dilute solutions of the substance in alcohol gave only a pale brown colour with ferric chloride, but more concentrated solutions produced a deep greenish blue which slowly faded. There was no precipitate with alcoholic neutral lead acetate for several hours.

When an alcoholic solution of the substance (0·05 g.) was treated with a solution of 2:4-dinitro-phenyl hydrazine (0·05 g.) in the same solvent (5 c.c.) containing two drops of concentrated hydrochloric acid, there was an almost immediate separation of a bright scarlet red crystalline solid. It was filtered and crystallised from a mixture of pyridine and glacial acetic acid. It formed bright red lance-shaped crystals melting at 270–72° with decomposition.

3:5:7:3′-*O-Tetramethyl myricetin* (*III*)

A solution of the tetramethyl quercetin aldehyde (0·5 g.) in N/2 sodium hydroxide (3·85 c.c.) was treated dropwise with vigorous shaking with 6% hydrogen peroxide (1·95 c.c.). The initial orange yellow solution changed to deep brown and became turbid. Pyridine was added to get a clear solution which was kept at the ordinary temperature for 2½ hours with occasional shaking and adding a few drops of pyridine to keep it clear. It was acidified with dilute hydrochloric acid when a small quantity of a yellow solid separated out. The acid solution was saturated with sodium chloride and shaken with ether when a bulky yellow precipitate was thrown out. It was filtered and washed with water. The ether extract on evaporation gave a little more of the substance. Yield 0·4 g. Crystallisation from a mixture of ethyl acetate and absolute alcohol gave pale yellow broad rectangular plates melting at 220–21°. (Found: C, 60·9; H, 5·1; $C_{19}H_{18}O_8$ requires C, 61·0; H, 4·8%). It was easily soluble in alcohol and acetone. The alcoholic solution gave an olive green colour with ferric chloride and a yellow precipitate with lead acetate. In 5% aqueous sodium hydroxide it dissolved to a bright orange coloured solution.

O-Hexamethylmyricetin (V)

The tetramethylmyricetin (III) (0·2 g.) was methylated in anhydrous acetone (20 c.c.), with dimethyl sulphate (0·5 c.c.) and potassium carbonate (3 g.). After refluxing for 3 hours, the solvent was distilled off, water was added to the residue and the white solid left behind was filtered and washed with water. Crystallisation from alcohol gave colourless flat needles melting at 155–56°. Mixed melting point with an authentic sample of myricetin hexamethyl ether was not depressed.

Myricetin (VI) was obtained by the demethylation of the tetramethyl ether (III) using hydriodic acid and acetic anhydride. The product crystallised from dilute acetic acid as yellow flat needles and rectangular plates, decomposed above 350° and had other properties and colour reactions identical with an authentic sample of myricetin.

3 : 5 : 7 : 3′-*Tetramethoxy*-4′ : 5′-*methylenedioxy-flavone*

(A) *By methylenation.*—A solution of tetramethyl myricetin (III) (0·2 g.) in acetone (20 c.c.) was treated with methylene sulphate (0·5 g.) and potassium carbonate (2 g.). After refluxing for 12 hours the mixture was filtered and the potassium salts washed with hot acetone. The filtrate was distilled off and the residue heated to boiling with 10% sodium hydroxide (10 c.c.). The white solid was filtered after cooling, washed well with water and crystallised from alcohol. It formed colourless rectangular plates melting at 214–15° (Found: C, 61·9; H, 5·0; $C_{20}H_{18}O_8$ requires C, 62·2; H, 4·7%). It was insoluble in aqueous alkali and did not give any colour with ferric chloride. A trace of the substance when heated with concentrated sulphuric acid (2 c.c.) and gallic acid (1 mg.) developed a stable brilliant bluish green colour.

(B) *By synthesis.*—An intimate mixture of ω : 4 :6-trimethoxy-2-hydroxy acetophenone (0·8 g.), myristicic anhydride (2 g.) and sodium salt of myristicic acid (1 g.) was heated under reduced pressure at 180° for 3 hours. The product was refluxed with 10% alcoholic potash (20 c.c.) for 20 minutes. The alcohol was distilled off and the residue treated with water. The undissolved solid was filtered, washed with 5% aqueous alkali followed by water and crystallised from alcohol. It formed colourless rectangular plates melting at 214–15° alone or in admixture with the sample described under (A).

SUMMARY

The most important example of ortho-oxidation from the point of view of the biogenesis of the anthoxanthins is the conversion of quercetin into

myricetin. *O*-3:5:7:3′-Tetramethyl quercetin has now been oxidised to *O*-tetramethyl-myricetin by the two stage process already explored in Part XV. The intermediate O-tetramethyl quercetin aldehyde and the final myricetin tetramethyl ether are obtained in satisfactory yields. From the latter 5-methoxykanugin, hexamethyl myricetin and myricetin have been obtained. These experiments could be taken as support for the multi-stage mechanism of ortho-oxidation. The appropriateness of the reagents from the point of view of biogenesis is discussed.

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STUDIES IN COLLOID OPTICS

Part I. The Sol-Gel Transformation of Agar-Agar Gels

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1. INTRODUCTION

THE transformation sol-gel or *vice versa* can be investigated by the methods of colloidal optics. The recent development in the field of Colloid-Optics, particularly in the hands of R. S. Krishnan,[1] has provided a very elegant method of investigating these problems.

The light scattering technique developed by R. S. Krishnan,[1] with the aid of a pair of double image prisms and the resulting four Tyndall cones has proved very useful indeed for studying the variations in the size and shape of colloid particles.

2. THE EXPERIMENTAL TECHNIQUE OF R. S. KRISHNAN

Unpolarised light from a uniformly illuminated slit S (Fig. 1) is condensed by a long focus lens L through the double image prism P_1, which is adjusted so as to give two tracks, one vertically below the other as at V and H. These two well separated beams are of equal intensity, the electrical vector in V being vertical and that in H being horizontal. At the focus of these two beams is placed the scattering medium under investigation, contained in a suitable rectangular cell. The two tracks are viewed at right angles to the incident direction (in the horizontal plane) through the second

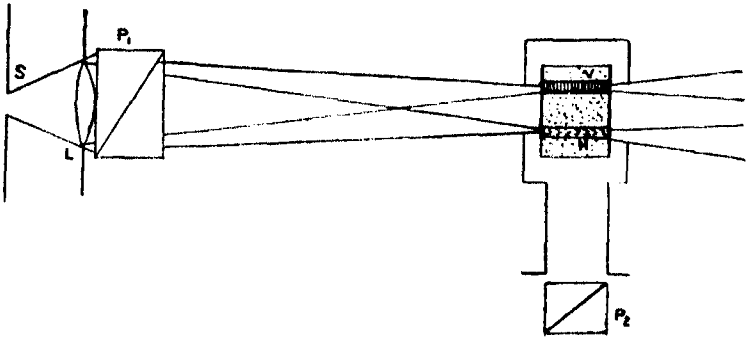


FIG. 1

double image prism P_2 which is crossed with respect to P_1. We now see four beams as shown in Fig. 2. The incident beam V is split up into two beams V_v and H_v the electric vector in them being ***vertical*** and ***horizontal*** respectively.

Similarly the incident beam H is split up into V_H and H_H (see Fig. 2) where the electric vectors are vertical and horizontal respectively.

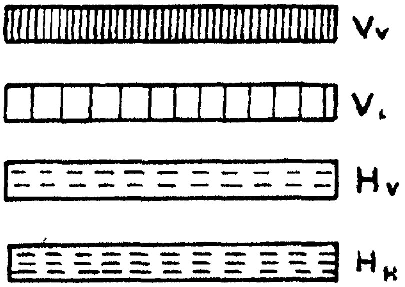


Fig. 2

As shown by R. S. Krishnan the principle of reciprocity is obeyed and the tracks V_H and H_v are always equal to each other in intensity.

The ratio $\frac{V_H}{H_H} = \rho_H$ is found to be a measure of the *size* of the scattering particles. Thus ρ_H is equal to 1 for particles of molecular dimensions and *decreases* in value as the size of the scattering particle increases.

Again, the ratio $\frac{H_v}{V_v} = \rho_v$ gives a measure of the anisotropy of the particle. It is *zero* for perfectly symmetrical particles and increases with the degree of asymmetry.

In the present investigation the optical method outlined above has been applied to the study of agar-agar dissolved in water in transformation from the ' Sol ' to the ' gel' state and *vice versa*. Krishnamurthi[2] had investigated this problem earlier in regard to agar-agar but he had used the then known technique of one incident beam of unpolarised light. The present investigation is a re-survey of the field covered by Krishnamurthi, using the new technique of R. S. Krishnan. Before discussing the variations of ρ_H and ρ_v the corresponding variations in the total scattering by a centimeter layer of the gel-sol with incident light unpolarised are described.

3. PREPARATION OF THE SOLS

A weighed quantity of agar-agar in the form of white fibres is kept in running water for about an hour. It is then boiled with distilled water in which it dissolves completely to form a turbid sol. The sol is then filtered hot several times to obtain a very clear transparent sol which is collected in a large test-tube. The test-tube is kept in a hot water-bath to prevent the sol from setting. This sol, when examined in a strong beam of convergent light shows no bright specks of light.

If the sol is maintained at a temperature above 40° C. for any length of time no appreciable change takes place. However, if the sol is below 40° C., a slow conversion from sol to gel takes place. The sol becomes increasingly viscous and ultimately sets to a gel. At the same time the intensity of the scattered light increases until the gel sets completely. The time taken by the sol to set to a gel decreases rapidly as the temperature of transformation falls below 40° C. Correspondingly the changes in the intensity of the scattered light occur faster and faster as the temperature of the experiment falls more and more below 40° C.

During the gel-sol transformation the changes noticed are not exactly the reverse of the sol-gel transformation. The tendency is for the gel state to persist indefinitely even at temperatures as high as 60° C. As the temperature is increased still higher the gel gradually transforms itself into the sol state without indicating any distinct temperature of transformation.

4. METHOD OF MEASURING THE INTENSITY OF SCATTERED LIGHT

(*a*) *Experimental arrangements for measuring intensity in the transverse direction.*—Light from a pointolite lamp is concentrated on a square aperture at S (see Fig. 3). It then passes through the converging lens L and is concentrated at P. The sol to be examined, kept in a test-tube is immersed in a rectangular glass cell containing clean water. The temperature of the sol is given by the thermometer T_1 and that of the water-bath W by the thermometer T_2. The whole of the test-tube is then painted dull black on the outside. There are just three rectangular apertures of suitable size, all in a horizontal plane, of which two serve for the entrance and exit of the beam of incident light, while the third aperture serves to observe the track of the incident beam at right angles to the direction of the incidence.

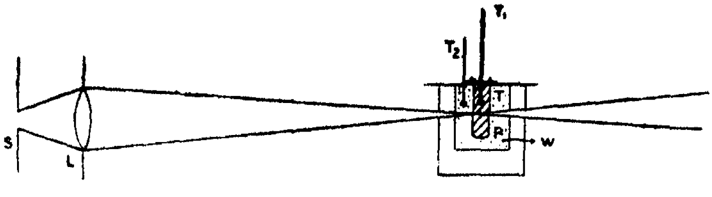


FIG. 3

The test-tube enters the water cell through an aperture in the cover and can be adjusted vertically. The water cell is 10 cm. by 10 cm. by 10 cm., made of good quality glass plates without optical strain. The glass sides are all painted dull black leaving only 3 transparent areas corresponding to those in the test-tube. The water cell is in turn surrounded by a wooden box the inner and outer sides of which are also painted dull black. This box also has three holes corresponding to the apertures in the test-tube and the glass cell. The transversely scattered light passes through the observational window and falls normally on a photo-cell which has a square aperture 1 cm. by 1 cm. and which is 10 cm. away from the track whose intensity is to be measuerd. As the photo-electric cell was most sensitive to red, a red filter was kept in front of the cell. The photocell and amplifier units are similar to those used by Ananthakrishnan,[3] where the out of balance current in a wheatstone bridge system is a function of the intensity of the radiation incident on the cell. The bridge is adjusted so that the micro-ammeter reads zero with no illumination. The reading of the micro-ammeter increases with the intensity of the scattered light.

(*b*) *Range of the photometer for linear response.*—To see in what range the response of the above photometer is linear the following subsidiary experiment was performed. The light passing through the lens L is made to pass through two nicol prisms, one of which can rotate on a divided circle about a horizontal axis. The light transmitted by these two nicols is allowed to fall on the photocell of the photometer. The bridge is adjusted so that the micro-ammeter reads zero when the nicols are crossed. The deflections in the microammeter for different rotations θ of the adjustable nicol away from its crossed position are then noted. The intensity I corresponding to a rotation θ of the nicol is given by

$I = I_0 \sin^2 \theta$, where I_0 is the maximum intensity when the nicols are in the parallel position.

Fig. 4 shows that the response of the photometer is linear in the range of current from 0 to 90 micro-amperes, which covers the range of readings when the photometer is used to measure the intensity of scattered light in our experiments.

(*c*) *Measurement of intensity I_0 of the incident beam.*—To express the scattered light as a fraction of the incident light, a knowledge of the intensity of the incident light I_0 is necessary. This, however, cannot be measured directly by the photo-cell unit as it is too intense. Therefore, the intensity of the incident beam was cut down to the working range by reducing the aperture of the pointolite to its minimum and introducing a strong filter

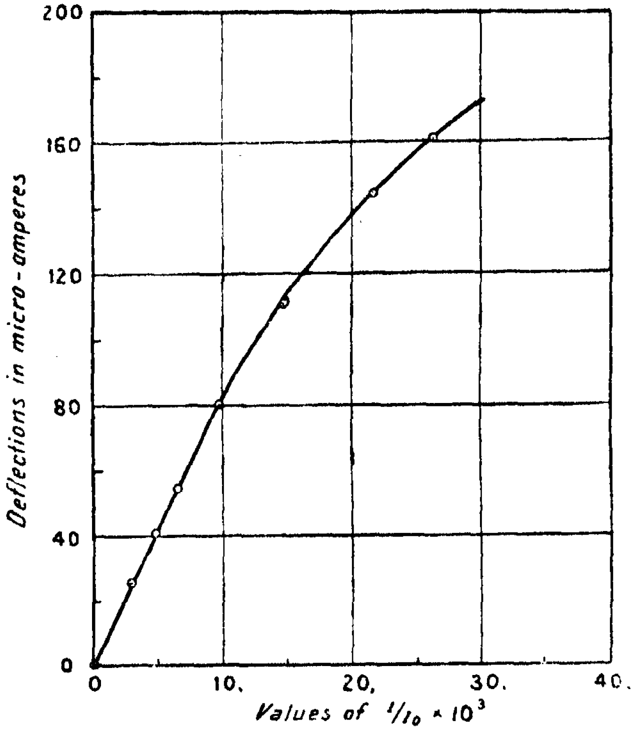


FIG. 4

of prussian blue, which has a strong absorption band in the red in front of the photo-cell. Various values of I transmitted through the filter for different concentrations of filter solution were measured in the range of the instrument. I, the intensity transmitted through the filter is given by

$I = I_0 \, 10^{-KC}$, where I_0 is the initial intensity and C is the concentration and K a constant so that $\log I = \log I_0 - KC$.

Fig. 5 is the linear graph of log I against C from which by extrapolation $\log I_0$ is obtained by putting $C = 0$.

From Fig. 5 we have $\log I_0 = 3 \cdot 76$ or $I_0 = 5754$ with minimum aperture width in terms of micro-ammeter readings in the range where the response is linear.

(*d*) *Estimation of the total scattering* (*over a solid angle* 4π) *by* 1 *cm. layer of the medium.*—In Fig. 6 let the horizontal track of the incident beam be AB along the x axis.

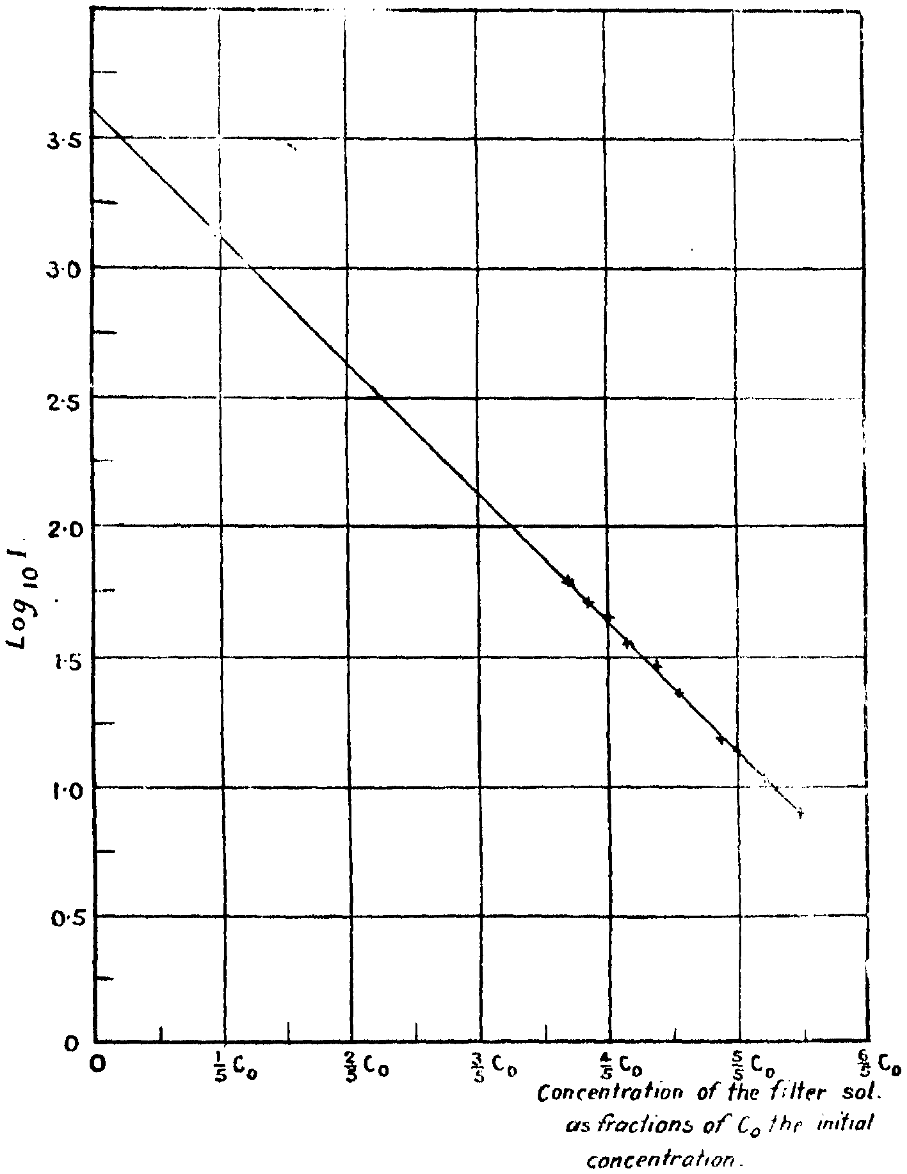


FIG. 5

XY is the horizontal plane. The intensity of the track AB is measured for values of θ varying from 0 to 180° with the help of the photometer. Fig. 7 shows the variation of intensity with azimuth θ. If we describe a sphere of radius r at the point O then zones can be described on the sphere corresponding to various intervals of θ, *e.g.*, θ_0 to θ_1, θ_1 to θ_2, θ_2 to θ_3, etc., etc.

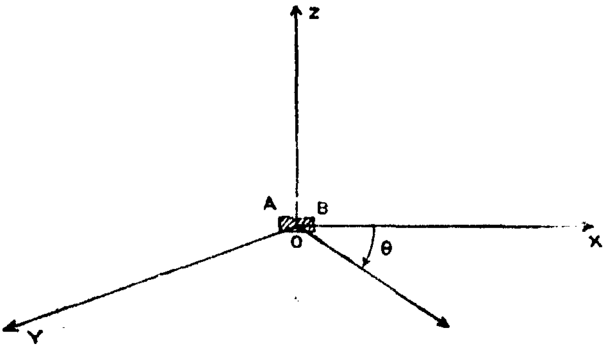
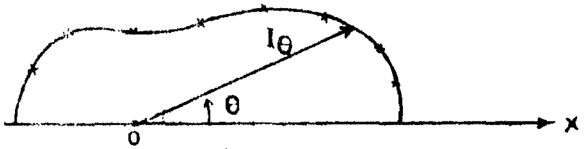


Fig. 6



Intensity distribution in the horizontal plane For gel set at 25 °C.

Fig. 7

Using the values of intensity given in Fig. 7 it is easy to compute the total intensity of the scattered light passing out of the whole sphere as

$$I_T = \Sigma I_\theta \text{ (zone) } = 2\pi \times 10^2 \times \Sigma I_\theta \sin\theta \, d\theta$$
$$= 20\pi \Sigma I_\theta \sin\theta$$

putting $d\theta = \frac{1}{10}$ radian, equal to the solid angle subtended by the aperture of the photo-cell.

This total intensity I_T can be expressed as a fraction $\frac{I_T}{I_0}$ of the incident beam. In Tables II to XI this value is given in the last column.

(*e*) *Measurement of the transmission by a layer of gel or sol.*—A beam of light passing through a diffusing medium undergoes depletion by scattering. Using the photometer it is easy to measure the transmission by a known thickness of the gel or sol. It is possible, therefore, to compare the total loss by scattering as estimated in (*d*) above with the loss in transmission.

An example of such comparison is given below:—

TABLE I

Light scattered by gel set at 25° C.

Concentration of agar-agar in the gel	Total light scattered by one centimetre layer over solid angle 4π	Loss in transmission per cm.
%	%	%
0·2	0·4	0·38
0·5	1·0	1·1
1·0	2·4	2·3
1·5	4·8	5·0

From the above it is seen that most of the loss of intensity during the passage through the medium is due to scattering. This loss, in the case of agar, for the concentrations dealt with, is also not so large as to affect the intensity of the Tyndall cone when viewed through the thin layer of the medium which usually intervenes between the track and the boundary of the containing vessel nearest to the observer.

5. MEASUREMENT OF DEPOLARISATION

The method of obtaining the four Krishnan components has already been described in para 2. The outside of the test-tube containing the gel under investigation is covered dull black excepting for three small square holes in a horizontal plane, two of which are in a straight line to allow the incident beam to pass through the gel while the third one is at right angles to the line joining the first two, for observations. The test-tube is held vertical so that only the upper one of the two incident beams (Fig. 1), namely *V*, passes through the gel, the lower H being cut off. Correspondingly, only the first and the third beams (Fig. 2) are obtained when viewed through the double image prism P_2. They are then observed through a nicol to which a divided circle is attached. The two successive positions of the nicol θ_1 and θ_2 at which the two beams appear to be of equal intensity are found. The ratio ρ_v of the third to the first beam is calculated by

$$\rho_v = \tan^2 \frac{(\theta_2 - \theta_1)}{2}.$$

The test-tube is then lowered slightly so that the upper beam V is cut off and the lower beam H only passes through the gel. The ratio ρ_H of the resulting two beams, namely (Fig. 2) the second to the fourth, is obtained in the same way as ρ_v. If the double image prism in the path of the incident beam is removed then we have a beam of unpolarised light passing through the scattering medium. If we now determine the ratio of the two components, seen through the double image prism on the observation side we get the value of ρ_u which is related to ρ_v and ρ_H as

$$\rho_u = \frac{1 + \frac{1}{\rho_H}}{1 + \frac{1}{\rho_v}}$$

We are therefore in a position to compare the observed values of ρ_u with those calculated from the value of ρ_H and ρ_v measured independently.

6. MEASUREMENTS OF ρ_v, ρ_H, ρ_u AND I IN AGAR-AGAR GELS OF VARIOUS CONCENTRATIONS

Measurements of ρ_v, ρ_H, ρ_u and I the intensity of transversely scattered light during the sol-gel transitions of agar-agar gels of concentrations 0·06%, 0·2%, 0·5%, 1% and 1·5% were recorded in a series of experiments.

(*a*) *Sol-gel transition.*—The sol prepared for the investigation is at first maintained at 90° C. for sometime by keeping the test-tube containing the sol in a hot water-bath and is then cooled to 80° C. by decreasing the temperature of the bath. It is then maintained at the constant temperature 80° C. for about 12 hours. At intervals of an hour the test-tube containing the sol is transferred to the water cell (Fig. 2) containing water at 80° C. for a short time and the intensity of the track viewed at right angles to the incident beam is measured with the photoelectric photometer. No change in intensity is noticed even after 12 hours. After measuring the intensity, the photo-cell unit is removed, and the double image prisms are inserted as in Fig. 1, to measure the values of depolarisation ρ_v, ρ_H, ρ_u. The above observations of intensity and polarisation are repeated at temperatures of 70° C., 60° C., 50° C., and 40° C., each time bringing the sol from 90° C. to the respective temperature and recording the variation of intensity with time keeping the particular temperature constant until no further change of intensity is noticed and finally the depolarisation values are also measured. No appreciable changes in intensity and depolarisation with time are noticed even after 12 hours at these temperatures above 40° C. Below 40° C., however, the observations are taken at each temperature down to 30° C. For each of these observations the sol is first cooled from 90° C. to 40° C. in the outside bath and the test-tube containing the sol at 40° C., is then transferred to the outer cell containing water at 40° C. The sol, along with the water in the outer cell is cooled at the uniform rate of one degree for every three minutes, to the particular temperature required which is maintained constant and observations of variations in intensity with time are taken until the intensities reach their maximum constant values and finally the depolarisations ρ_v, ρ_H, ρ_u are also recorded.

The sol first becomes highly viscous and then sets to a gel as time passes. It will be seen from Tables III to VII that there is no sensible change in the intensity from 90° C. to 38° C. For 37° C. and below the intensity increases with time until it reaches a maximum constant value at the particular temperature, time being measured from the instant the sol reaches the particular temperature. At lower temperatures the increase in intensity is more and more rapid and the limiting or saturation values of intensity are also reached earlier. Figs. 8 to 12 show the variation in intensity with time at different temperatures for gel concentrations of 0·06%, 0·2%, 0·5%, 1%, and 1·5%. The final values of intensity for a typical concentration are also shown by the portions OAB of the diagram in Fig. 13.

Gel-sol transformation.—The gel set at 25° C. is slowly heated to different temperatures and maintained at these temperatures until the values of intensity and depolarisation become steady. The curve CD in Fig. 13 shows the final steady value of intensity at each temperature during the gel-sol transition. Similar curves were obtained for other concentrations

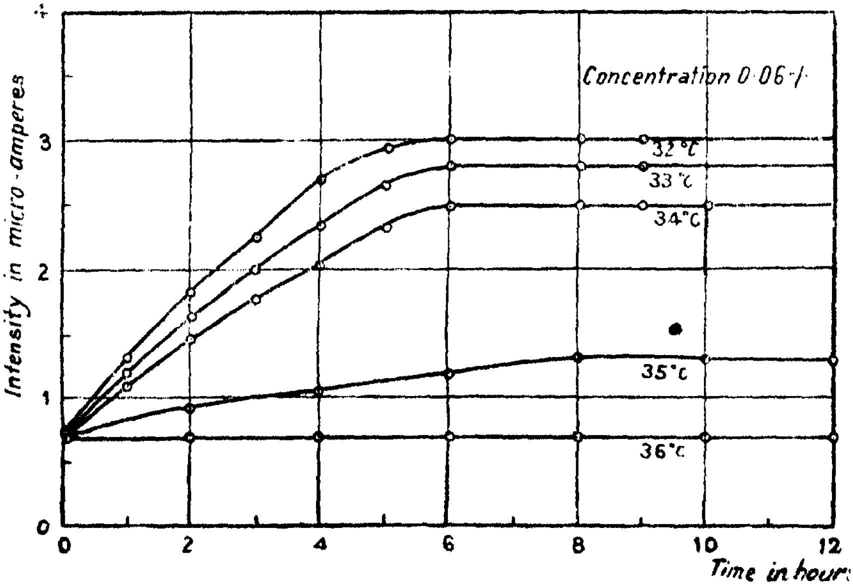


FIG. 8

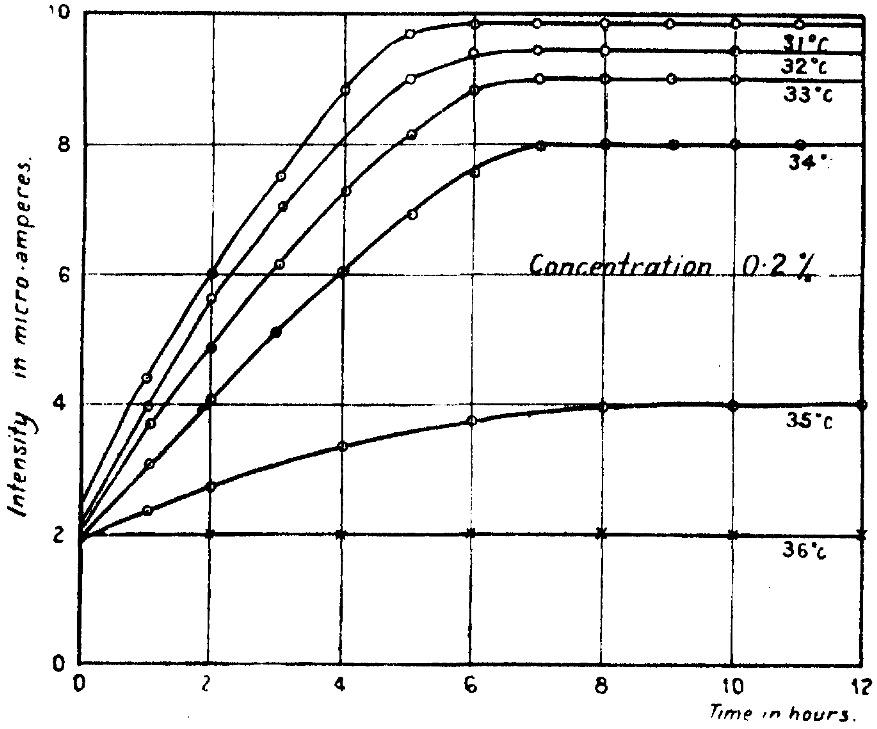

10
8
6
4
2
0
Intensity in micro-amperes.
0
2
4
6
8
10
12
Time in hours.
31°C
32°C
33°C
34°
35°C
36°C
Concentration 0·2 %

FIG. 9

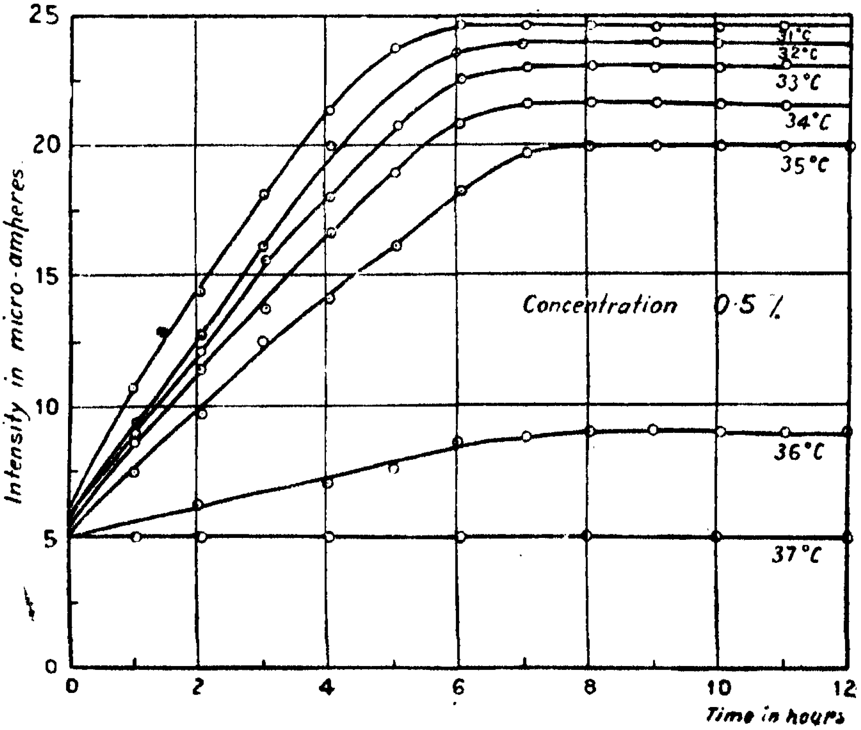
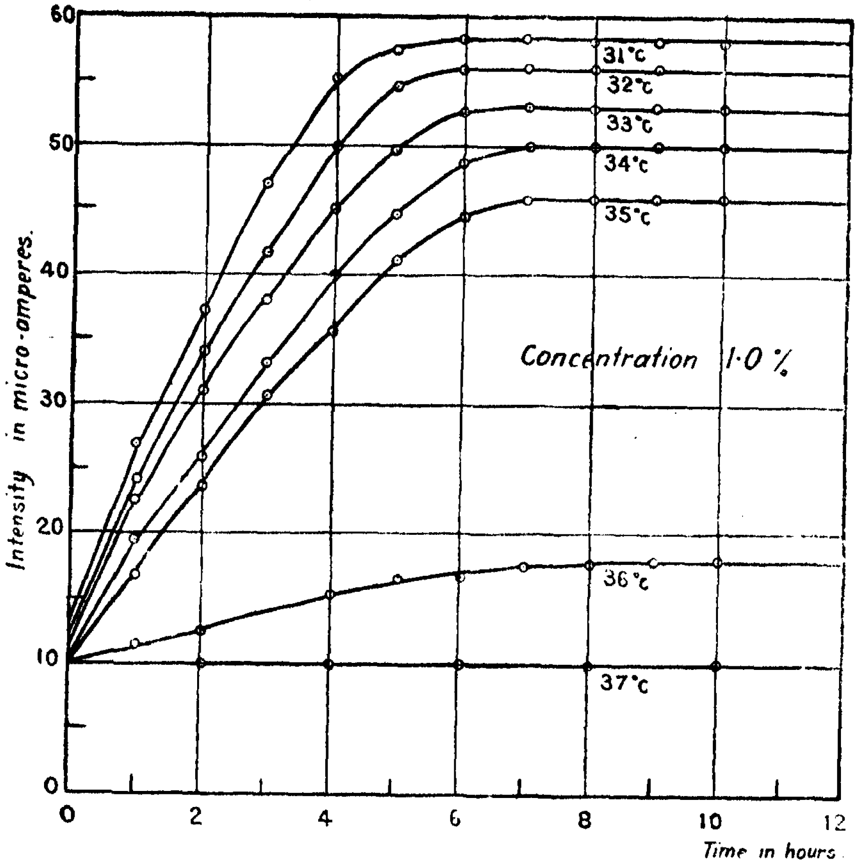
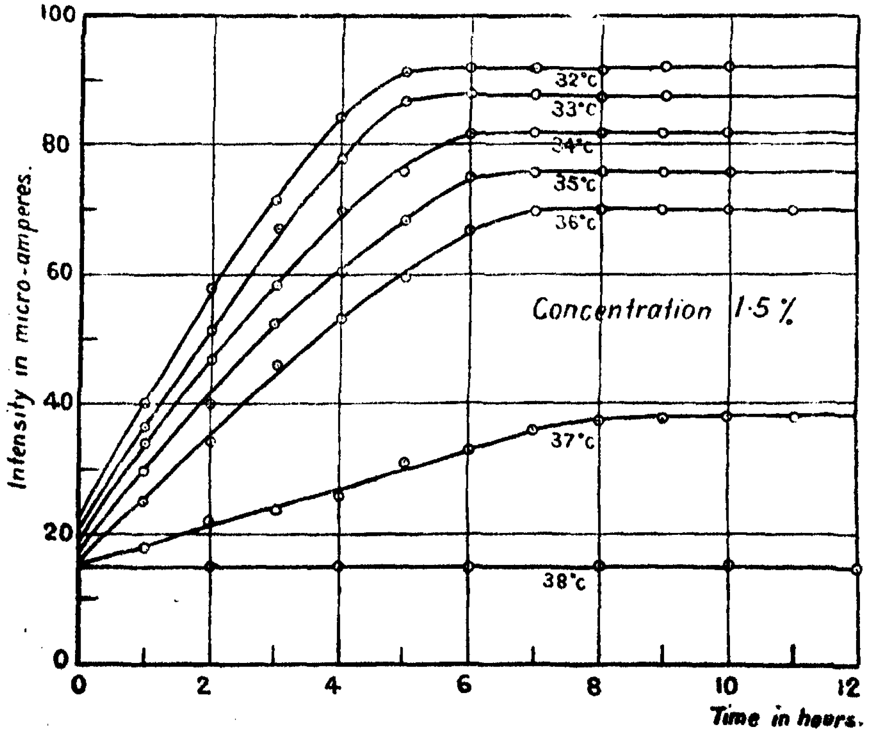

25
20
15
10
5
0
Intensity in micro-amperes
0
2
4
6
8
10
12
Time in hours
31°C
32°C
33°C
34°C
35°C
36°C
37°C
Concentration 0·5 %

FIG. 10



60
50
40
30
20
10
0
Intensity in micro-amperes.
0
2
4
6
8
10
12
Time in hours
31°c
32°c
33°c
34°c
35°c
36°c
37°c
Concentration 1·0 %

Fig. 11



100
80
60
40
20
0
Intensity in micro-amperes.
0
2
4
6
8
10
12
Time in hours.
32°c
33°c
34°c
35°c
36°c
37°c
38°c
Concentration 1·5 %

Fig. 12

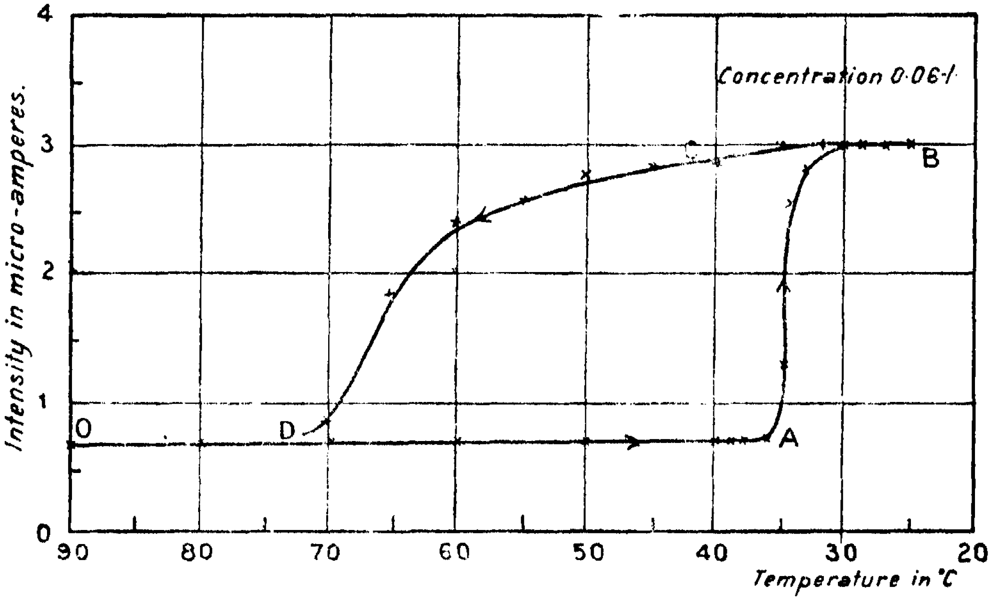


FIG. 13

also. The final steady values of depolarisations ρ_v, ρ_H, ρ_u at different temperatures during the gel-sol transition are recorded in Tables VIII to XII.

7. DISCUSSION OF RESULTS

No sensible changes of intensity or depolarisation with time are noticed at temperature above 40° C. for all concentrations studied. However, if the sols are maintained at constant temperatures below 40° C. for sufficiently long time, intensity and depolarisations change over gradually until they reach constant values which depend upon the temperatures. ρ_H, ρ_v, ρ_u and I recorded in Tables III to VII are the final steady values obtained at the various temperatures.

It can be seen from Tables III to XII that the calculated and observed values of ρ_u agree throughout the range investigated, thus verifying the Krishnan relations:

$$V_H = H_v \tag{1}$$

$$\rho_u = \frac{1 + \frac{1}{\rho_H}}{1 + \frac{1}{\rho_v}} \tag{2}$$

Variations in intensity during the transition from sol-gel are continuous showing that the gelation is a continuous process. The cooling curve

(Fig. 14) between 40° C. and 29° C. does not show any kink associated with sudden evolution or absorption of heat during the transition from sol to gel.

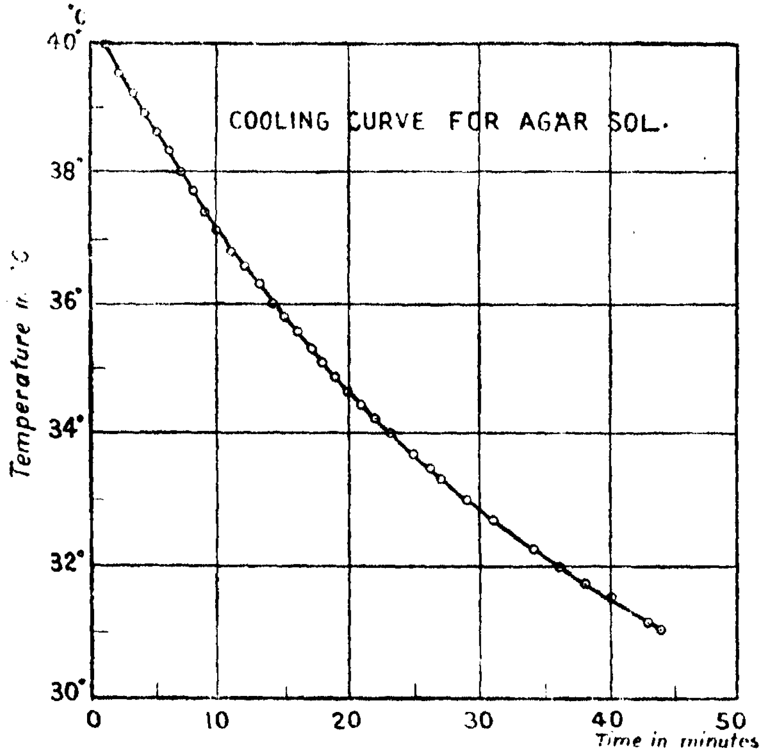


FIG. 14

TABLE II

Percentage of total light scattered (in all directions) in the sol and gel state, by agar-agar gels of different concentrations

Concentration	Light scattered in the sol state (temp. above 40° C.) I_s	Light scattered by gel set at 25° C. I_g
%	%	%
0·06	0·026	0·13
0·2	0·08	0·4
0·5	0·2	1·0
1·0	0·4	2·4
1·5	0·6	4·0

Variations in Intensity.—At temperatures above 40° C. the total amount of the light scattered in the sol state is directly proportional to the concentration (Table II), showing that size and shape distribution of the suspended particles is the same in sols of all concentrations. This can be seen to agree with the fact that the values of depolarisations ρ_v and ρ_H (Tables III to VII) are almost the same for all concentrations. In the gel state, however, the ratio $\frac{I_r}{I_s}$ increases with concentration. This increase can be seen to be due to the greater increase in the size and anisotropy of the particles in the gel state at higher concentrations as shown by the depolarisation values ρ_H and ρ_v recorded in Tables III to VII.

TABLE III

Concentration 0·06%

Temperature in °C.	ρ_H%	ρ_v%	(Cal.) ρ_u%	(Obs.) ρ_u%	Light scattered by 1 cm. layer of the medium
90	95	3·6	7·2	7·2	0·026 × 10^{-2}
70	95	3·6	7·2	7·2	0·026 ,,
50	95	3·6	7·2	7·2	0·026 ,,
40	95	3·6	7·2	7·2	0·026 ,,
38	95	3·6	7·2	7·2	0·026 ,,
37	95	3·6	7·2	7·2	0·026 ,,
35	85	2·6	5·6	5·7	0·052 ,,
34	75	1·7	4·0	4·1	0·102 ,,
33	70	1·5	3·8	3·7	0·100 ,,
32	70	1·5	3·8	3·7	0·118 ,,
31	67	1·35	3·4	3·4	0·130 ,,
25	67	1·35	3·4	3·4	0·130 ,,

TABLE IV

Concentration 0·2%

Temperature in °C.	ρ_H%	ρ_v%	(Cal.) ρ_u%	(Obs.) ρ_u%	Light scattered by 1 cm. layer of the medium
90	95	3·6	7·2	7·2	0·080 × 10^{-2}
70	95	3·6	7·2	7·2	0·08 ,,
50	95	3·6	7·2	7·2	0·08 ,,
40	95	3·6	7·2	7·2	0·08 ,,
38	95	3·6	7·2	7·2	0·08 ,,
37	95	3·6	7·2	7·2	0·08 ,,
35	85	2·7	5·8	5·7	0·16 ,,
33	70	1·9	4·5	4·6	0·36 ,,
32	67	1·7	4·2	4·2	0·38 ,,
31	65	1·6	4·0	4·0	0·40 ,,
25	65	1·6	4·0	4·0	0·40 ,,

TABLE V

Concentration 0·5%

Temperature in °C.	$\rho_H\%$	$\rho_v\%$	(Cal.) $\rho_u\%$	(Obs.) $\rho_u\%$	Light scattered by 1 cm. layer of the medium
90	95	3·6	7·2	7·2	0·2 × 10^{-2}
70	95	3·6	7·2	7·2	0·2 ,,
50	95	3·6	7·2	7·2	0·2 ,,
40	95	3·6	7·2	7·2	0·2 ,,
38	95	3·6	7·2	7·2	0·2 ,,
37	95	3·6	7·2	7·2	0·2 ,,
35	85	2·7	5·8	5·7	0·26 ,,
33	70	1·9	4·5	4·6	0·92 ,,
32	67	1·7	4·2	4·2	0·94 ,,
31	65	1·6	4·2	4·2	0·97 ,,
25	65	1·6	4·2	4·2	1·00 ,,

TABLE VI

Concentration 1·0%

Temperature in °C.	$\rho_H\%$	$\rho_v\%$	(Cal.) $\rho_u\%$	(Obs.) $\rho_u\%$	Light scattered by 1 cm. layer of the medium
90	95	3·6	7·0	7·2	0·4 × 10^{-2}
70	95	3·6	7·2	7·2	0·4 ,,
50	95	3·6	7·2	7·2	0·4 ,,
40	95	3·6	7·2	7·2	0·4 ,,
38	95	3·6	7·2	7·2	0·4 ,,
37	95	3·6	7·2	7·2	0·4 ,,
35	85	2·1	4·3	4·4	0·76 ,,
33	65	2·8	6·8	6·7	2·16 ,,
32	65	3·0	7·3	7·4	2·30 ,,
31	60	3·0	7·3	7·4	2·40 ,,
25	60	3·0	7·3	7·4	2·40 ,,

TABLE VII

Concentration 1·5%

Temperature in °C.	$\rho_H\%$	$\rho_v\%$	(Cal.) $\rho_u\%$	(Obs.) $\rho_u\%$	Light scattered by 1 cm. layer of the medium
90	95	4·0	8·0	8·0	0·6 × 10^{-2}
70	95	4·0	8·0	8·0	0·6 ,,
50	95	4·0	8·0	8·0	0·6 ,,
40	95	4·0	8·0	8·0	0·6 ,,
38	95	4·0	8·0	8·0	0·6 ,,
37	80	5·0	10·6	10·6	1·5 ,,
35	65	5·8	13·8	13·8	3·10 ,,
33	65	5·8	13·8	13·8	3·4 ,,
32	60	8·0	20·0	20·0	3·7 ,,
31	55	8·4	22·0	22·0	3·8 ,,
25	55	8·4	22·0	22·0	3·8 ,,

TABLE VIII

Concentration 0·06%

Temperature in °C.	$\rho_H\%$	$\rho_v\%$	(Cal.) $\rho_u\%$	(Obs.) $\rho_u\%$	Light scattered by 1 cm. layer of the medium
25	67	1·35	3·4	3·4	0·13 × 10^{-2}
30	67	1·35	3·4	3·4	0·13 ,
35	67	1·35	3·4	3·4	0·13 ,,
40	70	1·5	3·8	3·7	0·11 ,,
45	70	1·5	3·8	3·7	0·11 ,,
50	70	1·5	3·8	3·7	0·108 ,,
55	75	1·7	4·0	4·1	0·104 ,,
60	75	1·7	4·0	4·2	0·096 ,,
65	85	3·0	6·5	6·6	0·072 ,,
70	90	3·4	7·0	4·9	0·032 ,,

TABLE IX

Concentration 0·2%

Temperature in °C.	$\rho_H\%$	$\rho_v\%$	(Cal.) $\rho_u\%$	(Obs.) $\rho_u\%$	Light scattered by 1 cm. layer of the medium
25	65	1·60	4·0	4·0	0·40 × 10^{-2}
30	65	1·60	4·0	4·0	0·40 ,,
35	65	1·60	4·0	4·0	0·40 ,,
40	65	1·60	4·0	4·0	0·39 ,,
45	65	1·60	4·0	4·0	0·39 ,,
50	70	1·9	4·5	4·6	0·37 ,,
55	70	1·9	4·5	4·6	0·36 ,,
60	75	2·2	5·0	5·2	0·34 ,,
65	80	2·8	6·2	6·1	0·24 ,,
70	95	3·6	7·2	7·1	0·10 ,,

TABLE X

Concentration 0·5%

Temperature in °C.	$\rho_H\%$	$\rho_v\%$	(Cal.) $\rho_u\%$	(Cal.) $\rho_u\%$	Light scattered by 1 cm. layer of the medium
25	65	1·6	4·2	4·2	1·0 × 10^{-2}
30	65	1·6	4·2	4·2	1·0 ,
35	65	1·6	4·2	4·2	1·0 ,,
40	65	1·6	4·2	4·2	0·98 ,,
45	65	1·6	4·2	4·2	0·98 ,,
50	67	1·7	4·2	4·2	0·96 ,,
55	70	1·9	4·5	4·6	0·92 ,,
60	70	1·9	4·5	4·5	0·90 ,,
65	90	3·4	7·0	7·0	0·46 ,,
70	95	3·6	7·2	7·2	0·24 ,,

TABLE XI

Concentration 1·0%

Temperature in °C.	ρ_H%	ρ_v%	(Cal.) ρ_u%	(Obs.) ρ_u%	Light scattered by 1 cm. layer of the medium
25	60	3·0	7·3	7·4	2·4 × 10^{-2}
30	60	3·0	7·3	7·4	2·4 ,,
35	60	3·0	7·3	7·4	2·4 ,,
40	60	3·0	7·3	7·3	2·35 ,,
45	60	3·0	7·3	7·3	2·35 ,,
50	65	3·0	7·3	7·3	2·30 ,,
55	65	3·0	7·3	7·3	2·30 ,,
60	65	2·8	6·8	6·7	2·15 ,,
65	75	3·1	7·0	7·2	1·04 ,,
70	90	3·4	7·2	7·2	0·55 ,,

TABLE XII

Concentration 1·5%

Temperature in °C.	ρ_H%	ρ_v%	ρ_u%	ρ_u%	Light scattered by 1 cm. layer of the medium
25	55	8·4	22·0	22·0	3·8 × 10^2
30	55	8·4	22·0	22·0	3·8 ,,
35	60	8·0	20·0	20·0	3·7 ,,
40	60	8·0	20·0	20·0	3·65 ,,
45	60	8·0	20·0	20·0	3·65 ,
50	60	8·0	20·0	20·0	3·60 ,,
55	65	5·8	13·8	14·0	3·4 ,,
60	65	5·8	13·8	13·8	2·8 ,,
65	75	5·4	12·0	11·9	2·0 ,,
70	90	4·2	8·5	8·6	0·8 ,,

Variations in ρ_H.—The second columns in Tables III to VII show that ρ_H decreases with decrease in temperature suggesting that the size of the particles for gels set at lower temperatures is bigger. It can also be seen that ρ_H decreases with concentration at low temperatures showing that for gels set at the same low temperature the size of the particles increases with concentration.

Variations in ρ_v.—The changes occurring in ρ_v with decrease in temperature are very interesting and occur as follows for different ranges of concentration.

(1) For sols of concentration 0·06%, 0·2% and 0·05%, ρ_v gradually decreases with temperature.

(2) For 1% sol ρ_v first decreases and then increases as the temperature is decreased.

(3) For 1·5% sol ρ_v gradually increases with temperature.

This suggests that in the first case the particles tend to become more symmetrical with decrease in temperature while in the second they tend to grow more symmetrical with decrease in temperature at first but assymmetry sets in with further lowering in the temperature. At 1·5% concentration the increase in assymmetry of the particle starts right from the beginning.

Mechanism of sol-gel transformation in agar-agar as suggested by the above results.—A consideration of the above mentioned variations in intensity, ρ_H and the three types of variations of ρ_v at the different ranges of concentration suggests that we have to deal here with two distinct phenomena. First of all we have the solute particles of small size initially, but tending to increase in size rapidly with the fall of temperature, as one approaches the range of temperatures associated with the sol-gel transformation. This process may occur in two stages. In the first stage (*a*) the particle tends to develop a cloud of H_2O molecules which surround it without however actually entering its structure. During this initial stage the intensity of the scattered light does not start increasing though the medium increases in viscosity. In the next stage of swelling; (*b*) we have also the actual physical swelling of the solute particle itself, somewhat analogous to what happens in osmosis. During this second stage, the intensity of scattering increases rapidly. In any case it is clear that during the stages (*a*) to (*b*) the individual particle undergoes an increase of size which tends to make it more symmetrical as is shown by the decrease in ρ_v. The later *increase* in ρ_v with further fall of temperature must be associated with aggregation or coagulation of swelled particles with a tendency to form increasingly unsymmetrical groups. This tendency becomes more pronounced at the higher concentration and indeed starts there at the very outset, as is the case with the highest concentration of 1·5%. Work on similar lines with gelatin gels is in progress.

SUMMARY

The transmission from sol to gel and *vice versa* in agar-agar gels has been investigated by means of the new experimental technique of R. S. Krishnan. Intensity distribution of the light scattered by a one centimeter layer of the scattering medium in the horizontal plane with incident unpolarised light has been measured by means of an electronic photometer during the various stages of the transition, and hence the total light scattered in all directions by a centimetre layer of the scattering medium during the transition has been calculated and expressed as a fraction of the incident intensity.

The depletion of the light transmitted through various thickness of the gels has also been measured and shown to be equal to the total light scattered by the gel. The detailed study of the variations in intensity and depolarisations during the various transitions from sol to gel and gel to sol suggest,

(1) The R. S. Krishnan relation:

$$\rho_u = \frac{1 + \frac{1}{\rho_H}}{1 + \frac{1}{\rho_v}}$$

holds throughout the range investigated.

(2) The transition from sol to gel is characterised by distinct stages.

(*a*) The solute particle first appears to develop a cloud of H_2O molecules round itself which results in an increase in the viscosity without any sensible change in the light scattering capacity of the gel.

(3) The actual particle size then increases as is indicated by the great increase in the light scattering capacity as well as the decrease in the value of ρ_H as compared with the sol. The values of ρ_v indicate that:

(*a*) The particles grow more symmetrical as their size increases for concentrations of 0·06%, 0·2%, and 0·5%.

(*b*) The particles first tend towards symmetry and later grow more and more unsymmetrical with incrase in size for the concentrations of 1% while,

(*c*) The tendency for the particles to grow more unsymmetrical with increase in size exists from the very start for concentrations of 1·5% or more.

ACKNOWLEDGEMENT

In conclusion, I wish to express my deep gratitude to Dr. L. A. Ramdas, Director of Agricultural Meteorology, for suggesting me the problem, for guidance and encouragement during the course of the investigation and for providing the necessary facilities for the work. My thanks are also due to Mr. R. S. Kale for building the photo-electric unit used in the present investigation.

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ANTHRAQUINONE SERIES

Part II. Halogenated Aminoanthraquinones and Indanthrones

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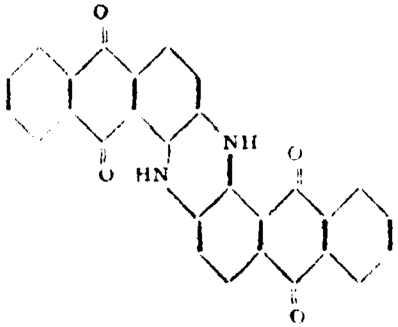
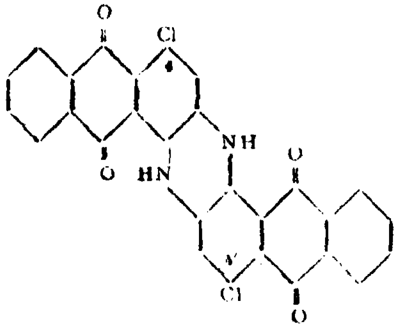
Although indanthrone (I) was the first anthraquinone vat dyestuff discovered as early as 1901, indanthrone and its derivatives have continued to be among the most important anthraquinone vat dyes produced in large quantities by most of the dyemakers. Indanthrone possesses excellent fastness properties to all agencies other than chlorine, in which case it undergoes a greening of shade, probably due to oxidation to the azine. The halogenated derivatives of indanthrone, especially the dichloro derivatives, possess improved fastness to chlorine, and a series of halogenated indanthrones are now commercially available, examples being Caledon Blue RCS, GCD, BCD, GCPS and Alizanthrene Blue RC (ICI), and Indanthrene Blue GCD, BC, GC and RCL (I.G.).

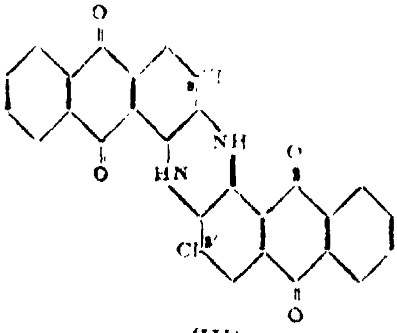
Conflicting statements have been made in the literature regarding the constitution of the commercial chlorinated indanthrones and their methods of preparation. According to Fraser-Thomson[1] Caledon Blue GCD is



(I)



(II)



(III)

largely the 4:4′-aichloroindanthrone (II) obtained by chlorination of indanthrone with gaseous chlorine or with sulphuryl chloride. The 3:3′-orientation of the chlorine atoms is assigned by Rowe[2] who gives the following methods of preparation: (1) chlorination of indanthrone with sulphuryl chloride or benzoyl chloride, (2) the action of nitric and hydrochloric acids on indanthrone and (3) synthesis from 3-chloro-1-bromo-2-aminoanthraquinone. According to Fraser-Thomson[1] and Rowe,[3] Caledon Blue RC is 3:3′-dichloroindanthrone (III) prepared synthetically, as it cannot be prepared by direct halogenation. In Colour Index[2] the dye is formulated as a trichloro-derivative of indanthrone, prepared by the action of antimony pentachloride or sulphuryl chloride on indanthrone. It is also prepared by the action of chlorine on indanthrone suspended in sulphuryl chloride, thionyl chloride or antimony pentachloride· Rowe[3] has described the preparation of Soledon Blue 2RCS, which is the tetrasulphuric ester of 3:3′-dichlorotetrahydroindanthrone by the oxidation of 3-chloro-2-aminoanthrahydroquinone disulphuric ester with hypochlorite or lead peroxide. Indanthrene Blue GC and Caledon Blue GC are mentioned in Colour Index[2] as the 3:3′-dibromo-derivatives of indanthrone.

Indanthrene Blue GCD has been regarded as being identical with Caledon Blue GCD. According to Rowe[3] the former is largely 4:4′-dichloroindanthrone (II) obtained by direct chlorination. Indanthrene Blue BC, stated[4] to contain more chlorine atoms than the dichloro derivative and probably prepared by direct chlorination, has been described as identical with Caledon Blue RC in Colour Index.[2] The authentic methods for the preparation of the IG dyes are, however, now available.[5] Indanthrene Blue GCD is prepared by direct chlorination by passing chlorine in a solution of indanthrone in 91·5% sulphuric acid at 50–55° in the presence of a small quantity of manganese dioxide till the chlorinated product has a chlorene content of 5–8%. Indanthrene Blue BC is the higher chlorinated product, obtained by carrying the chlorination further till the chlorine content is 13·8 to 14% chlorine (Calc. for dichloroindanthrone: Cl, 13·9%).

While a series of halogenated indanthrones have become commercially available and numerous processes for their preparation have been patented, the mode of action of different chlorinating agents is largely unknown. According to Fraser-Thomson[4] and Rowe[3] direct halogenation of indanthrone attacks both the 3:3′-and the 4:4′-positions, but chiefly the latter. The 3:3′-dihalogeno-derivatives cannot be prepared in pure form by direct halogenation and hence have to be obtained synthetically.[3] Methods of direct chlorination of indanthrone which claim to lead to the 3:3′-dichloro derivative have, however, been reported in patents.[6] Substitution in the 3:3′-positions is stated to scarcely affect the shade of indanthrone, while substitution in the 4:4′-positions causes greening of the attractive reddish blue shade of indanthrone.

It is obvious that, while preparation from a halogenated intermediate, in which the orientation of the halogen atoms is definite, will give a chloroindanthrone of authentic constitution, the position of the chlorine atoms in a product obtained by the direct chlorination of indanthrone needs to be proved. The present work was undertaken with a view to determining the constitution of commercial chloroindanthrones and investigating the orientation of the dichloroindanthrones prepared by chlorination of indanthrone with antimony pentachloride and sulphuryl chloride.

Antimony pentachloride was found to be a vigorous chlorinating agent, two chlorine atoms being readily introduced in indanthrone by reaction in boiling nitrobenzene for 15 minutes. It was observed that even when excess of antimony pentachloride is used and the reaction carried out for 3 hours, no further chlorine could be introduced. It would appear that antimony pentachloride specifically attacks two positions in indanthrone, and no further chlorination can then be effected. When dichloroindanthrone prepared with antimony pentachloride (subsequently referred to as IIA), the dichloroindanthrone prepared through the azine which will be described later, and 3:3′-dichloroindanthrone obtained from its solubilised derivative Soledon Blue 2RCS, were treated with antimony pentachloride, no further chlorination took place, so that the presence of two chlorine atoms in the indanthrone molecule prevents further action of antimony pentachloride.

The action of sulphuryl chloride was found to be markedly different from that of antimony pentachloride. When excess of sulphuryl chloride was used, the chlorination did not stop with the introduction of two chlorine atoms but proceeded further. By carefully controlling the experimental conditions a dichloroindanthrone was prepared.

Scholl and Berblinger[7] have prepared a dichloroindanthrone by the action of hydrochloric acid on anthraquinoneazine, the product being claimed to be 4:4′-dichloroindanthrone without conclusive supporting evidence. Seeking such proof, dichloroindanthrone prepared according to Scholl and Berblinger[7] was treated with hydrazine, so that the dihydrazinoindanthrone may be produced, but the reaction was not successful.

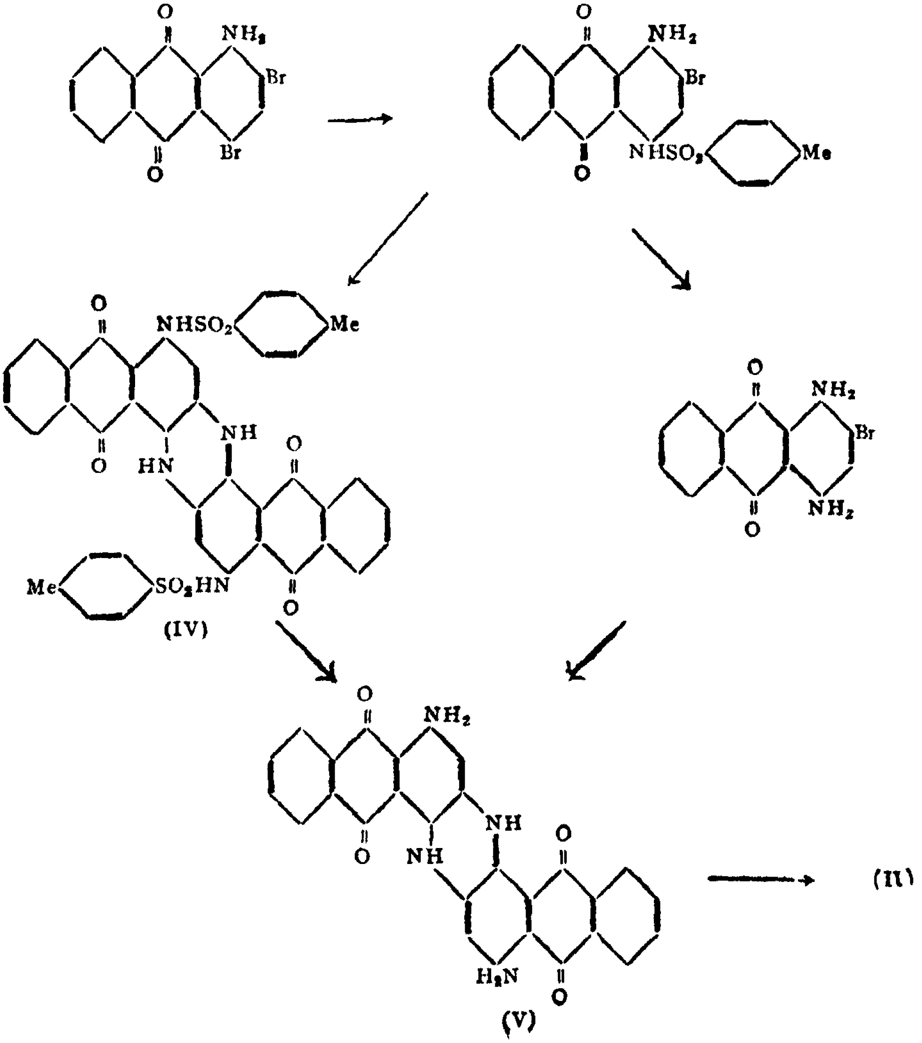
Atack and Soutar[8] have described the preparation of 3:3′-dichloroindanthrone by self-condensation of 3-chloro-1-bromo-2-aminanthraquinone (m.p. 235°), which was obtained from 3-chloro-2-aminoanthraquinone by bromination in nitrobenzene. They prepared the latter, for which they have quoted m.p. of 221°, by chlorination of 2-aminoanthraquinone with gaseous chlorine in acetic acid or nitrobenzene. As 3-chloro-2-aminoanthraquinone prepared by unambiguous methods[8] melts at 310°, while 1-chloro-2-aminoanthraquinone[6] melts at 237°, it appeared likely that Atack and Soutar actually obtained the latter, rather than the 3-chloro-compound. Their chloro-bromo-2-amino anthraquinone and its self condensation product would, therefore, be 1-chloro-3-bromo-2-aminoanthraquinone and 3:3′-dibromoindanthraquinone respectively. Direct chlorination of 2-aminoanthhraquinone generally leads first to 3 chloro- and then to 1:3-dichloro-2-aminoanthraquinone, and to get 1-chloro-2-aminoanthraquinone it is necessary to acetylate 2-aminoanthraquinone before chlorination.[9, 10] Fyfe[11] has, however, prepared 1-chloro-2-aminoanthraquinone by direct chlorination of 2-aminoanthraquinone in nitrobenzene, chlorobenzene and acetic acid without previously acetylating the amino group. When 2-aminoanthraquinone was chlorinated with sulphuryl chloride, 1-chloro-2-aminoanthraquinone (m.p. 237°) was obtained which was characterised by preparing its acetyl derivative (m.p. 241°) and comparison with authentic specimens of 1-chloro-2-aminoanthraquinone and its acetyl derivative.[12] Bromination of 1-chloro-2-aminoanthraquinone thus obtained gave 1-chloro-3-bromo-2-aminoanthraquinone, which melts at 238°, comparing well with the product prepared by Atack and Soutar[7] (m.p. 235°) and claimed as 3-chloro-1-bromo-2-aminoanthraquinone. Self-condensation of 1-chloro-3-bromo-2-aminoanthraquinone now prepared gave 3:3′-dibromoindanthrone as expected.

For the purposes of the present work 3:3′-dichloroindanthrone[13] was then synthesised by the self-condensation of 3:3′-dichloro-2-aminoanthraquinone.[9]

One of the methods for the synthesis of 4:4′-dichloro-indanthrone would be from the hitherto unknown 1:4-dichloro-2-aminoanthraquinone obtainable by the cyclisation of *o*-(2′:5′-dichloro-4′-amino) benzoylbenzoic acid. Attempts to prepare the latter acid by condensation of phthalic anhydride with 2:5-dichloroacetanilide in the presence of anhydrous aluminium chloride proved unsuccessful as 2:5-dichlorophenylphthalamic acid was obtained instead .of the desired acid. Another route explored was through 4-chloro-2-bromo-1-aminoanthraquinone. Attempts to brominate 2-bromo-1-aminoanthraquinone gave 2:4-dichloro-1-aminoanthraquinone instead of the desired product. The only recorded method for the preparation of 2:4-dichloro-1-aminoanthraquinone is due to Guhelmann *et al.*[14]

who obtained it synthetically from *m*-dichlorobenzene and phthalic anhydride in four steps; they were unsuccessful in obtaining it by direct chlorination by methods analogous to those used for the preparation of 2:4-dibromo-1-aminoanthraquinone. It is remarkable that contrary to the experience of the above workers direct chlorination of 1-aminoanthraquinone in glacial acetic acid gave 2:4-dichloro-1-aminoanthraquinone in excellent yield.[16] The constitution of the latter was confirmed by the preparation of 1:2:4-trichloroanthraquinone by the Sandmeyer reaction and by deamination to 1:3-dichloroanthraquinone.

The utility of 2:4-dichloro-1-aminoanthraquinone, which has now become readily available, as a dyestuff intermediate was investigated. Thus



the N-benzoyl derivative was prepared, but was found to have poor substantivity to cotton. Condensation with *p*-toluidine and aniline gave 2-chloro-1-amino-4-*p*-toluidinoanthraquinone and 2-chloro-1-amino-4-anilinoanthraquinone which on sulphonation would lead to acid dyes. 2: 4-Dichloro-1-aminoanthraquinone on diazotisation and coupling with β-naphthol gave a reddish brown dye. Syntheses of anthraquinone-acridones from the dichloro derivative are also being studied.

4-Chloro-2-bromo-1-aminoanthraquinone was prepared by the bromination of 4-chloro-1-aminoanthraquinone, but it did not give 4:4′-dichloroindanthrone by self-condensation. Attempts to replace the hydroxyl groups in 4:4′-dihydroxyindanthrone (Indanthrene Blue 5G) by chlorine atoms by the action of phosphorus pentachloride were also unsuccessful.

Another route for the synthesis of 4:4′-dichloroindanthrone was then investigated. 2-Bromo-1-amino-4-*p*-toluenesulphonamidoanthraquinone[17] on condensation with itself gave the new 4:4′-di-*p*-toluenesulphonamidoindanthrone (IV) in 76 per cent. yield. Hydrolysis of (IV) with concentrated sulphuric acid gave a bluish green vat dye similar in properties to 4:4′-diaminoindanthrone (V), but with 1·5% lower nitrogen content. It was, however, found that (V) could be readily synthesised through 1:4-diamino-2-bromoanthraquinone.[18] Treatment of (V) with concentrated sulphuric acid also resulted in a loss in nitrogen indicating a partial hydrolysis of the amino groups during the hydrolysis of (IV). Attempts to replace the amino groups by chlorine by the Sandmeyer reaction proved unsuccessful.

When 2-aminoanthraquinone was chlorinated with gaseous chlorine in nitrobenzene a new trichloro-2-aminoanthraquinone (m.p. 216°) was obtained. Fries and Hartmann[14] obtained 1:3:4-trichloro-2-hydroxyanthraquinone by treating 2-aminoanthraquinone with gaseous chlorine in fuming hydrochloric acid and acetic acid and subsequently treating the reaction product with sodium acetate. By analogy the trichloro derivative obtained can be formulated as 1:3:4-trichloro-2-aminoanthraquinone. Self-condensation of the trichloro derivative did not give 3:4:3′:4′-tetrachloroanthraquinone, but a brown dye containing less chlorine content.

The specific α-chlorinating action of antimony pentachloride has been observed by Steiner[19] who obtained 1:4:5:8-tetrachloroanthraquinone by chlorination of anthraquinone with this reagent. While substitution of the α-positions (4, 5, 8, 4′, 5′ and 8′) in indanthrone in direct chlorination can be regarded as more likely than the β-positions on account of the higher activity of the α-positions, there is no reason to assume, as Fraser-Thomson[4] and Rowe[3] have done, that the 4:4′-positions are first substituted and then the 3:3′-positions, leaving the other available α-positions unsubstituted. Since antimony pentachloride unlike sulphuryl chloride is specific in introducing two atoms of chlorine, it is reasonable to regard the dichloroindanthrone (IIA) as a pure α:α′-disubstituted derivative, and probably the 4:4′-dichloro derivative, on the basis of its greater resistance to azine formation on treatment with oxidising agents as discussed later. The chlorinated indanthrones obtained by direct halogenation with sulphuryl chloride or gaseous chlorine are probably indanthrones substituted chiefly in the 5, 8, 5′ and 8′-positions. Since a halogen atom substituted in the α-position in the anthraquinone molecule is much more reactive than a β-chlorine atom, chlorine atoms substituted in the α-positions in indanthrone should be more reactive than those in the β-positions. The lability of the chlorine atoms in dichloroindanthrones prepared by direct chlorination, 3:3′-dichloroindanthrone, and the commercial chloroindanthrones, towards boiling alkaline sodium hydrosulphite solution was then tested. It was found that the chlorine atoms in (IIA) were the least stable, as much as 57% of chlorine being lost after this treatment. At the other end of the scale was the synthetic 3:3′-dichloroindanthrone which lost about 24% chlorine, under identical conditions. Dehalogenation of (IIA) and 3:3′-dichloroindanthrone by heating with copper bronze resulted in a loss of 32% and 25% chlorine respectively. The above experiments give some supporting evidence to the exclusive α-orientation in (IIA).

Attempts to synthesise 4:4′-dichloroindanthrone unambiguously which could then be compared with (IIA), have so far been unsuccessful, and another approach to a solution of the problem was to convert (IIA) into di-*p*-toluenesulphonamidoindanthrone or diaminoindanthrone for comparison with the synthetic specimens (IV) or (V) respectively. Ammonolysis of (IIA) to give the diamino derivative in the presence of arsenic trioxide under pressure proved unsuccessful. Reaction of (IIA) with *p*-toluenesulphonamide resulted in partial substitution of the chlorine atoms by *p*-toluenesulphonamido groups. 3:3′-Dichloroindanthrone did not react with *p*-toluenesulphonamide under these conditions. While the synthesis of the *p*-toluenesulphonamido derivative from (IIA) could not be accomplished, the higher reactivity of the chlorine atoms in (IIA) as compared to 3:3′-dichloroindanthrone has given further evidence as regards their α-orientation in (IIA).

Pure chloroindanthrones were isolated from commercial Caledon Blue RC and GCD, Soledon Blue 2RCS and Indanthrene Blue BC and GCD, which represent the more important members of the group of commercial chloroindanthrones. The purified dyes were compared with the chloroindanthrones now prepared, the comparison relating to (1) the shade on cotton yarn, (2) colour reactions,[20, 21] (3) fastness to chlorine, (4) chlorine content, and (5) stability of chlorine to alkali and sodium hydrosulphite.

The crystallised dyes isolated from Caledon Blue RC and GCD, Soledon Blue 2RCS, and Indanthrene Blue BC analysed for dichloroindanthrone (Cl = 13·9%), but purified Indanthrene Blue GCD contained only 5·8% chlorine (calc. for monochloroindanthrone 7·5%). Although most of the properties of the different chlorinated indanthrones were practically identical they could nevertheless be distinguished by the different reactivity of the chlorine atoms and by the colour reaction recently described by Derrett-Smith and Gee.[21]

The chlorine atoms in (IIA) were least stable to treatment with alkaline hydrosulphite, while those in the 3:3′-dichloroindanthrone were most stable, all the other chloroindanthrones, occupying intermediate positions between these two extremes. The dichloroindanthrone obtained through the anthraquinoneazine does not appear to be the 4:4′-dichloro derivative as claimed by Scholl and Berblinger,[6] being comparable in the stability of the chlorine to 3: 3′-dichloroindanthrone. While the greater lability of the chlorine atoms in (IIA) in comparison with 3:3′-dichloroindanthrone suggests α-orientation, the test is beset with experimental difficulties and for the present can only be regarded as a rough distinction between α- and β-orientation of chlorine atoms in indanthrone.

Derrett-Smith and Gee[21] have recently reported a colour reaction, involving treatment of the dyed yarn successively with acid permanganate and acid hydrogen peroxide, for distinguishing vat dyes such as halogenated indanthrones, dibenzanthrones and certain grey and black dyes which could not be distinguished by their earlier tests.[20] The chlorinated indanthrones are oxidised to different extents to the yellow azine by treatment with the potassium permanganate and hydrogen peroxide solutions, and it is possible to distinguish them by the colour changes observed in this test. Thus Indanthrene Blue RSN, GCD, BC and 3GT, Caledon Blue RN, 3GCT and GCPS which give greenish yellow to green colour changes are distinguished from Indanthrene Blue GT, BCD and BCS, Indanthrene Brilliant Blue RCL and Caledon Blue GCS, GCDS, RCS, BCD, 2R, Caledon Brilliant Blue 2RC, Soledon Blue 2RC and Alizanthrene Blue RC which give a bluish green to greenish blue colour change. On examination of the chlorinated indanthrones by this test, it was found that Indanthrene Blue GCD and BC, which are dichloroanthrones prepared by the action of chlorine in sulphuric acid,[5] and dichloroindanthrone prepared by sulphuryl chloride gave a greenish yellow to yellow colour change while Caledon Blue GCD, RC, the dichloroindanthrone from Soledon Blue RC and 3: 3′-dichloroindanthrone synthesised by us gave greenish blue to bluish green colour changes. The resistance to colour changes in 3:3′-dichloroindanthrone in this test is probably due to the proximity of chlorine atoms to the imino groups of indanthrone which retard oxidation of the latter to the azine. Caledon Blue RC, GCD and the parent vat dye from Soledon Blue RC are likewise resistant to oxidation and are probably 3:3′-dichloroindanthrone. The dichloroindanthrone (IIA) is distinguished from the other dichloroindanthrones obtained by direct chlorination by its similarity to 3:3′-dichloroindanthrone in this test. It is, however, different from the latter in the greater activity of the chlorine atoms which has been referred to earlier. If (IIA) is constituted as 4:4′-dichloroindanthrone and the other direct chlorinated indanthrones as indanthrones substituted largely in the 5, 8, 5′, 8′-positions, the similarity of (IIA) to 3:3′-dchloroindanthrones in Derret-Smith and Gee's test can be readily accountea for, as the substitution of chlorine atoms in the 4:4′-postions should retard the oxidation of indanthrone to the azine to a greater extent than substitution in the more remote 5, 8, 5′, 8′-positions, although to a less extent than substitution in the 3:3′-positions. The reactivity of the chlorine atoms in (IIA) and the other direct chlorinated indanthrones should be of the same order as they are all chiefly α-substituted derivatives.

Further and more conclusive evidence regarding the orientation of chlorine in the chlorinated indanthrones is being sought by a study of the degradation products[22] and by a synthesis of 4:4′-dichloroindanthrone.

EXPERIMENTAL

Chlorination of indanthrone with antimony pentachloride.—Antimony pentachloride (3·2 c.c.; 4·4 mols) was added to a suspension of indanthrone (2·5 g.; 1 mol) in nitrobenzene (20 c.c.), and the mixture was boiled for 15 minutes. After cooling, the mixture was filtered and the residue was washed with alcohol and benzene and then treated with hot 1:1 hydrochloric acid to remove residual antimony. The residue was washed with water, dried (2·8 g.) and then crystallised from quinoline when blue needles of dichloroindanthrone (IIA) were obtained (Found: N, 5·4; Cl, 13·8. $C_{28}H_{12}O_4N_2Cl_2$ requires N, 5·5; Cl, 13·9%).

Dichloroindanthrone prepared from Soledon Blue 2RCS, the dichloroindanthrone obtained through the azine which will be described later and

(IIA), when further treated with antimony pentachloride as above, remained unaffected.

Chlorination of indanthrone with sulphuryl chloride.—The action of sulphuryl chloride on indanthrone under various conditions was studied in order to determine the conditions for obtaining dichloroindanthrone. It was found that the optimum conditions were to heat a suspension of indanthrone (2 g.) in nitrobenzene (15 c.c.) with sulphuryl chloride (1 c.c.; 2·7 mols) with mechanical agitation for 2 hours. The mixture was cooled, filtered and the residue was washed with alcohol and then with water. Since the chloroindanthrone was partly oxidised to the azine it was treated with a solution of sodium hydrosulphite, filtered, washed and dried. Crystallisation from high boiling pyridine bases (b. p. 235–245°) gave dichloroindanthrone as blue needles (Found: Cl, 14·0. $C_{28}H_{12}O_4N_2Cl_2$ requires Cl, 13·9%.) The dichloroindanthrone was similar to (IIA) in its properties and colour reactions although there were certain minor differences which will be described later. When the molar proportion of sulphuryl chloride was increased to 3·2 and 3·8 mols., the chlorine content of the product increased to 15·9 and 16·9% irespectively; trichlorindanthrone requires Cl, 19·5%).

Action of hydrochloric acid on anthraquinoneazine.—Indanthrone (5 g.) was treated with potassium nitrate (4·5 g.) and concentrated sulphuric acid (41 c.c.) for 75 minutes and then diluted with acetic acid (166 c.c.) at 0°. The precipitated golden yellow anthraquinoneazine was washed successively with glacial acetic acid, 5% caustic soda solution and water. The azine (4·5 g.) was boiled with concentrated hydrochloric acid (50 c.c.) for 6 hours, during which the yellow azine changed to the blue chloroindanthrone. The chloroindanthrone obtained was washed free from hydrochloric acid and dried (4·5 g.) (Found: Cl, 3·7. $C_{28}H_{13}O_4N_2Cl$ and $C_{28}H_{12}O_4N_2Cl_2$ require Cl, 7·5 and 13·9% respectively). The chloroindanthrone was again subjected to the above treatment when the chlorine content increased to 8%. A third treatment gave a product containing 12·3% chlorine which, on further treatment, gave dichloroindanthrone crystallising from high boiling pyridine bases as blue needles (Found: N, 5·4; Cl, 13·8. $C_{28}H_{12}O_4N_2Cl_2$ requires N, 5·5; Cl, 13·9%.)

1-*Chloro-2-aminoanthraquinone.*—A solution of sulphuryl chloride (1·2 c.c.) in nitrobenzene (25 c.c.) was added dropwise during 4 hours to a boiling solution of 2-aminoanthraquinone (2 g.) and anhydrous sodium acetate (0·9 g.) in nitrobenzene (15 c.c.). After further boiling under reflux for 1 hour the mixture was worked up as usual. The crude product (2·3 g.), m.p. 225°, when crystallised from alcohol, gave orange needles of 1-Chloro-2-aminoanthraquinone (VI), m.p. 237–238°, undepressed when mixed with a specimen (m.p. 236–38°) prepared by hydrolysis of 1-chloro-2-acetamidoanthraquinone (VII) (m.p. 240–42°) obtained by the chlorination of 2-acetaminoanthraquinone.[12] The acetyl derivative, m.p. 241–242°, prepared from (VI) was identical with (VII).

1-*Chloro-3-bromo-2-aminoanthraquinone.*—A solution of bromine (1·2 c.c.) in glacial acetic acid (10 c.c.) was added gradually to a solution of 1-chloro-2-aminoanthraquinone (2 g.) in acetic acid (100 c.c.) at room temperature under stirring. After addition of more glacial acetic acid (50 c.c.), the mixture was boiled under reflux for 2 hours. The crystalline compound (2·35 g.), which separated on cooling the mixture to 0°, was recrystallised from glacial acetic acid when 1-chloro-3-bromo-2-aminoanthraquinone separated in yellowish brown needles, m.p. 238° (Found: N, 4·0; Cl, 10·4; Br, 23·9. $C_{14}H_7O_2NClBr$ requires N, 4·2; Cl, 10·6; Br, 23·8%). A solution of the amine (2g.) in acetic anhydride (10 c.c.) was acidified with a drop of concentrated sulphuric acid, vigorously shaken for 15 minutes and then diluted with water. The product after crystallisation from alcohol gave 1-chloro-3-bromo-2-acetamidoanthraquinone as shining yellow plates, m.p. 185–186° (Found: Cl, 9·5; Br, 20·8. $C_{16}H_9O_3NClBr$ requires Cl, 9·4; Br, 21·0).

3 : 3′-*Dibromoindanthrone.*—1-Chloro-3-bromo-2-amino-anthraquinone (1·7 g.), anhydrous sodium acetate (0·5 g.), anhydrous copper sulphate (0·1 g.) and nitrobenzene (20 c.c.) were boiled under reflux for 4 hours. After cooling, the mixture was filtered, washed with nitrobenzene, alcohol and hot water and dried (0·9 g.). On crystallisation from high boiling pyridine bases (b.p. 235–245°), 3 : 3′-dibromoindanthrone separated as lustrous blue needles with a copper reflex.

1 : 3 : 4-*Trichloro-2-aminoanthraquinone.*—Dry chlorine was passed through a suspension of 2-aminoanthraquinone (15 g.) in nitrobenzene (40 c.c.) at room temperature under vigorous stirring for 3 hours. The amine gradually dissolved and the golden yellow solution obtained was steam distilled to remove nitrobenzene and the residue obtained was dried and washed with ether. The product (6·6 g.) was crystallised from glacial acetic acid when 1 : 3 : 4-trichloro-2-aminoanthraquinone separated as pale yellow needles, m.p. 216° (Found: N, 4·3; Cl, 32·6. $C_{14}H_6O_2NCl_3$ requires N, 4·2; Cl, 32·5%). The amine (2 g.) when boiled with acetic anhydride (10 c.c.) for 2 hours gave 1 : 3 : 4-trichloro-2-acetamidoanthraquinone which crystallised from glacial acetic acid in pale yellow needles, m.p. 263° (Found:

N, 3·7; Cl, 29·0. $C_{16}H_8O_3NCl$ requires N, 3·8; Cl, 28·9%.) Self-condensation of the trichloroaminoanthraquinone gave noncrystallisable brown dye containing 12·5 per cent. chlorine as against the required value of 24·5 per cent. for tetrachloroindanthrone.

3 : 3′-*Dichloroindanthrone.*—1 : 3-Dichloro-2-aminoanthraquinone[9] (2 g.), anhydrous sodium acetate (1 g.), anhydrous copper sulphate (20 mg.) and nitrobenzene (15 c.c.) were boiled together for 24 hours. The mixture was cooled, filtered, and the residue was washed successively with boiling glacial acetic acid, alcohol and water. The product (0·4 g.) on crystallisation from high boiling pyridine bases gave blue needles of 3 : 3′-dichloroindanthrone (Found: N, 5·6; Cl, 13·8. $C_{28}H_{12}O_4N_2Cl_2$ requires N, 5·5; Cl, 13·9%).

2 : 5-*Dichlorophenylphthalamic acid.*—2 : 5-Dichloroacetanilide (2 g., 1 mol) and phthalic anhydride (1·5 g., 1 mol) were added to a molten mixture of anhydrous aluminium chloride (10 g.) and sodium chloride (3 g.). The reaction mixture was heated for one hour under stirring at 180°, cooled, mixed with dilute hydrochloric acid and then filtered. The residue was extracted with 5% sodium hydroxide solution and the extract on acidification gave 2 : 5-dichloro-phenylphthalamic acid as a white precipitate. On crystallisation from dilute alcohol, colourless needles, m.p. 169° were obtained (Found: N, 4·4; Cl, 23·1. Acid equivalent, 312. $C_{13}H_8ONCl_2{\cdot}CO_2H$ requires N, 4·5; Cl, 22·9%. Acid equivalent, 310). On hydrolysis with concentrated sulphuric acid at 100° phthalic acid was obtained.

2 : 4-*Dichloro*-1-*aminoanthraquinone.*—(1) Dry chlorine prepared from potassium permanganate (2 g.) and concentrated hydrochloric acid (20 c.c.) was passed at a moderate rate through a suspension of 2-bromo-1-aminoanthraquinone[17] in glacial acetic acid (100 c.c.) kept vigorously stirred at 100°. As a test portion contained insufficient halogen, the mixture was further treated with the same amount of chlorine under similar conditions. The reaction mixture was poured into water and the precipitate was collected, washed, dried and crystallised from alcohol, when reddish brown needles of 2 : 4-dichloro-1-aminoanthraquinone were obtained, m.p. 205°. Guhelmann *et al.*[18] give m.p. 205–6° (Found: N, 4·9; Cl, 24·2. Calculated for $C_{14}H_7O_2NCl_2$ N, 4·8; Cl, 24·3%).

(2) Dry chlorine from potassium permanganate (10 g.) and concentrated hydrochloric acid (75 c.c.) was passed in a suspension of 1-aminoanthraquinone (13·5 g.) in glacial acetic acid (140 c.c.) at such a rate that the reaction was completed in 3 hours. During the reaction the mixture was kept well agitated and the temperature was maintained at 100°. The reaction mixture was finally boiled for a short time and then cooled to 0°. The

product which separated was washed with a little acetic acid and dried, m.p. 202° (15 g.). The mother liquor on concentration gave a second crop of the product (1 g.). On recrystallisation from alcohol reddish brown needles of 2:4-dichloro-1-aminoanthraquinone were obtained, m.p. 205°.

A solution of 2:4-dichloro-1-aminoanthraquinone (2 g.) in acetic anhydride (30 c.c.) and concentrated sulphuric acid (2 drops) was vigorously shaken for 30 minutes and then diluted with water, when the *acetyl* derivative was obtained. Crystallisation from glacial acetic gave orange needles which did not melt upto 360° (Found: N, 4·3; Cl, 21·2. $C_{16}H_9O_3NCl_2$ requires N, 4·2; Cl, 21·3%).

2:4-*Dichloro*-1-*benzamidoanthraquinone.*—The amine (2 g.) was dissolved in benzoyl chloride (10 c.c.) and at 100° the solution was acidified with two drops of concentrated sulphuric acid. After agitation for 30 minutes, the *benzoyl* derivative was obtained on dilution with water, and it crystallised from solvent naphtha in yellow needles, m.p. 217° (Found: N, 3·4; Cl, 17·8. $C_{21}H_{11}O_3NCl_2$ requires N, 3·5; Cl, 17·9%). The red alkali-hydrosulphite vat had practically no affinity for cotton.

2:4-*Dichloroanthraquinone*-1-*azo*-β-*naphthol.*—2:4-Dichloro-1-aminoanthraquinone (1·5 g.) was dissolved in glacial acetic acid (50 c.c.) and concentrated hydrochloric acid (1 c.c.) was added and the mixture was boiled for a few minutes. After cooling to room temperature, sodium nitrite (0·4 g.) was added and the mixture was left for 15 minutes and then coupled with an alkaline solution of β-naphthol (0·9 g.) below 25°. After leaving overnight the *azo dye* was filtered, precipitated from concentrated sulphuric acid and finally crystallised from pyridine, when reddish brown needles were obtained, m.p. 241° (Found: N, 6·1. Cl, 15·7. $C_{24}H_{12}O_3N_2Cl_2$ requires N, 6·3; Cl, 15·9%).

2-*Chloro*-1-*amino*-4-(-*p-toluidino*)-*anthraquinone.*—2:4-Dichloro-1-aminoanthraquinone (3·0 g., 1 mol), p-toluidine (5 g.; 5 mols), anhydrous sodium acetate (1 g.), anhydrous copper sulphate (50 mg.), precipitated copper (50 mg.) and amyl alcohol (30 c.c.) were boiled under reflux for 7 hours, and the mixture was worked up as usual. The crude product (2·9 g.; yield 81%), m.p. 231–33°, crystallised from solvent naphtha in violet plates, m.p. 238–39°.

2-*Chloro*-1-*amino*-4-*anilinoanthraquinone.*—2: 4-Dichloro-1-aminoanthraquinone (1·45 g.), aniline (2·3 c.c.), anhydrous sodium acetate (0·5 g.), anhydrous copper sulphate (50 mg.), precipitated copper (50 mg.) and amyl alcohol (30 c.c.) when boiled under reflux for 10 hours gave the *anilino derivative* which crystallised from solvent naphtha in reddish blue plates, m.p.

232–33° (Found: N, 8·1; Cl, 10·3. $C_{20}H_{13}O_2N_2Cl$ requires N, 8·0; Cl, 10·2%).

4-*Chloro-2-bromo-1-aminoanthraquinone.*—A solution of bromine (1·2 c.c.; 1 mol) in glacial acetic acid (10 c.c.) was gradually added to a solution of 4-chloro-1-aminoanthraquinone (5 g.; 1 mol) in acetic acid (100 c.c.) at room temperature with mechanical agitation. The mixture was boiled under reflux for 2 hours and then cooled to 0°. The product which separated (6·1 g.) was recrystallised from glacial acetic acid when the *bromo derivative* separated as red needles, m.p. 209° (Found: N, 4·0; Cl, 10·5; Br, 24·0. $C_{14}H_7O_2NCl$ requires N, 4·2; Cl, 10·6; Br, 23·8%). A solution of the compound (1·5 g.) in benzoyl chloride (10 c.c.) when treated with a drop of concentrated sulphuric acid at 100° and agitated for 15 minutes gave the *benzoyl derivative* which crystallised from solvent naphtha in pale yellow needles, m.p. 228° (Found: N, 3·0; Cl, 8·2; Br, 18·0. $C_{21}H_{11}O_3NClBr$ requires N, 3·2; Cl, 8·1; Br, 18·2). The benzoyl derivative gave a red alkaline hydrosulphite vat which had very little substantivity for cotton.

4-*Chloro-1-benzamidoanthraquinone.*—4-Chloro - 1 - aminoanthraquinone was benzoylated in the presence of sulphuric acid. The benzoyl derivative crystallised in golden yellow needles from solvent naphtha, m.p. 240° (Found: N, 3·7, Cl, 9·7. $C_{21}H_{12}O_3NCl$ requires N, 3·9; Cl, 9·8).

4:4′-*di-p-toluenesulphonamidoindanthrone* (*IV*).—2-Bromo-1-amino-4-*p*-toluenesulphonamidoanthraquinone (2·81 g.), prepared according to Ullmann and Eiser,[17] fused sodium acetate (0·6 g.), anhydrous copper sulphate (0·12 g.) and nitrobenzene (40 c.c.) were boiled under reflux for 48 hours. The mixture was filtered while hot and then washed successively with nitrobenzene, boiling toluene, benzene and finally with methyl alcohol. The residue was extracted with hot water, leaving 4:4′-di-*p*-toluenesulphonamidoindanthrone as dark greenish blue needles possessing a reddish blue lustre (1·76 g.; yield 76%) (Found: N, 7·0%. $C_{42}H_{28}O_8N_4S_2$ requires N, 7·2%). The compound gave a pale blue shade on cotton from a blue alkaline hydrosulphite vat which was only partly exhausted at the end of 45 minutes of dyeing. When the compound (1·4 g.) was treated with concentrated sulphuric acid (25 c.c.) at 50° for 3 hours it gave 4:4′-diaminoindanthrone as a greenish blue precipitate which dyed a bluish green shade on cotton. The latter, however, contained only 10·3% nitrogen as against 11·9% required for diaminoindanthrone indicating a loss of nitrogen during the hydrolysis of the *p*-toluenesulphonamido derivative.

4:4′-*Diaminoindanthrone.*[18]—A mixture of 2-bromo-1:4-diaminoanthraquinone[17] (1·0 g.), copper bronze (0·1 g.), fused sodium acetate (0·5 g.)

and nitrobenzene (8·4 c.c.) was vigorously boiled under reflux for 6 hours at 230–240°. The mixture was filtered while hot and the residue was extracted repeatedly with boiling toluene till the filtrate was nearly colourless. The residue was washed with methyl alcohol with water and then boiled with concentrated hydrochloric acid. It was washed free from acid and dried, when 4 : 4′-diaminoindanthrone was obtained as an olive black product (0·62 g.) giving a bluish green shade on cotton (Found: N, 11·9. $C_{28}H_{16}O_4N_4$ requires N, 11·9%). On treatment with concentrated sulphuric acid at 50–60° for 3 hours the nitrogen content of the product decreased to 9·2%.

Purification of commercial chloroindanthrones.—The general method of purification was to remove water-soluble diluents (mainly sodium bicarbonate), then boil with 5% hydrochloric acid wash and crystallise from high boiling pyridine bases, when the pure dye usually separated as blue needles. Soledon Blue 2RCS was oxidised with hydrochloric acid and sodium nitrite to dichloroindanthrone which was then purified by crystallisation. Estimation of sulphuric acid liberated by hydrolysis indicated the dye to be the sodium salt of the tetrasulphuric ester of dichlorotetrahydroindanthrone.

Comparison of chloroindanthrones.—The pure chloroindanthrones isolated from the commercial dyes and the pure dyes now prepared were compared with regard to the properties mentioned earlier, as well as the following, and the results are summarised in Table I.

TABLE I

Dye	% Chlorine content	% Chlorine content after alkali hydrosulphite treatment	% Chlorine loss	Colour reactions.[20, 21]				Acid $KMnO_4$ and H_2O_2
				Acid vat	Alkaline vat	Sulphuric acid	Nitric acid group	
Indanthrone Blue GCD ..	5·8	4·94	14·8	Violet	Blue	Brown		Green-yellow
Indanthrone Blue BC ..	13·0	5·83	55·1	Blue	Blue	Greenish Brown	D	Yellow-green
Caledon Blue GCD ..	13·9	8·64	37·8	do	do	do	do	Blue-green
Caledon Blue RC ..	13·9	8·62	38·0	do	do	do	do	do
Vat dye from Soledon Blue 2RCS	13·9	10·42	25·0	do	Greenish blue	do	do	do
3 : 3′-Dichloroindanthrone	13·9	10·60	23·7	do	do	do	do	do
Dichloroindanthrone (IIA)	13·8	5·91	57·2	do	Blue	do	do	do
Dichloroindanthrone from sulphuryl chloride	14·0	7·58	45·8	do	do	do	do	Yellow-green
Dichloroindanthrone from the azine	13·9	10·61	23·7	do	Greenish blue	do	do	Blue-green

Colour reactions.—The colour reactions described by Bradley and Derrett-Smith[20] and Derrett-Smith and Gee[21] for the characterisation of vat dyes were examined (Table I).

Stability of the chlorine in the dyes.—The pure, finely powdered dye (0·5 g.) was treated with a solution of sodium hydroxide (3·0 g.) and sodium hydrosulphite (2·5 g.) in water (250 c.c.) at 60–65° for 3 hours. After cooling, the dye was recovered by air-oxidation, washed till free from chlorides and sulphates, dried and its chlorine content was then determined.

We are indebted to the Council of Scientific and Industrial Research under whose auspices part of the work was carried out, the Imperial Chemical Industries, Ltd., for gifts of chemicals and Mr. T. S. Gore for some of the microanalyses recorded in the paper.

SUMMARY

Attempts to determine the orientation of the chlorine atoms in some of the commercial chlorinated indanthrones and in the dichloroindanthrones prepared by the action of antimony pentachloride and sulphuryl chloride on indanthrone and by the action of hydrochloric acid on anthraquinone-azine are described. The higher reactivity of the chlorine atoms in the direct chlorinated indanthrones suggests α-orientation. The dichloro-indanthrone (IIA) from antimony pentachloride is distinguished from the other chloroindanthrones obtained by direct chlorination by its greater resistance to azine formation on treatment with oxidising agents. The 4:4′-orientation is, therefore, suggested for the chlorine atoms in (IIA), and substitution in the 5, 8, 5′, 8′ positions in the other direct chlorinated indanthrones. Antimony pentachloride was found to be specific in introducing two chlorine atoms in indanthrone. 4:4′-Di-*p*-toluenesulphonamido-indanthrone (IV) has been synthesised.

2:4-Dichloro-1-aminoanthraquinone has been prepared by an improved method and its utility as a dyestuff intermediate has been studied. A few other halogenated aminoanthraquinones and their acyl dervatives which do not appear to have been described in literature have been synthesised.

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C. V. Raman

SIR C. V. RAMAN ON HIS SIXTIETH BIRTHDAY

On the 7th of November 1948, Sir C. V. Raman attained the age of sixty. It was an occasion for public rejoicings all over India. For, more than any other Indian, he has raised the intellectual prestige of the country and placed her well and truly on the scientific map of the world. The respect, esteem, and affection with which he is regarded by his friends and scientific colleagues found expression in the many messages and greetings which reached him from far and near on his birthday.

It is a matter of the deepest satisfaction that the advancing years have laid their hands on him very lightly indeed. During the ten years that have elapsed since the publication by the Academy of the Jubilee Volume on the occasion of his fiftieth birthday, his achievement in research, as evidenced by the stream of published work from his laboratory, has been greater than ever, while the range of his scientific interests has continually expanded. Far from retiring from active research or changing over to less strenuous pursuits, Sir C. V. Raman has consistently refused offers of positions which would have diverted him from his chosen path as an investigator.

During the past few years, he has also perfected plans that would enable him to devote the rest of his life, and the whole of his time, to the pursuit of his scientific interests without having to suffer distractions. On a magnificent site overlooking Bangalore and the surrounding country for over thirty miles on all sides, an imposing structure of granite has been raised which will house a Research Institute of which he will be the permanent Director. The library, the lecture theatre, and the museum of the Institute, have been fitted up and the research laboratories are now being equipped. With the additional advantage of the climate of Bangalore, one of the finest in the world, the Raman Research Institute, on being fully equipped, will certainly attract many distinguished workers from all over the world.

It will be the earnest wish of all that Sir C. V. Raman lives many more years and enjoys the health and strength needed to achieve his aims in the fullest measure.

S. Ramachandra Rao.

SIR C. V. RAMAN AS PHYSICIST AND TEACHER

A BRIEF review of the investigations in the field of crystal physics, carried out by Sir C. V. Raman and his pupils, is given in the next article of the present issue. We only wish to indicate here a few characteristic features of the scientific work of Sir C. V. Raman, his approach to research, and his relationships with his pupils.

The most obvious characteristic is his great passion for physics coupled with an intense enthusiasm and volcanic energy. Even the most casual observer cannot fail to miss the fire in his sparkling eyes which seem to radiate this energy, and to be animated by the dynamic force of an active brain. He lives for his work as few men do, and by his exceptional tenacity of purpose, and of hard work in the pursuit of research he has set a shining example to others.

He has a deep insight into physical processes, and an intuitive sense of physical reality. He has often shown the ability to illuminate a whole subject with a few crucial ideas. His highest work shows the inevitable simplicity of all great work, and has been achieved by spontaneously taking the significant step at the right moment. He possesses in a remarkable degree the gift of seizing the vital point from apparently trivial observations. This genius for picking out the true significance of what to others would be an unimportant detail, and transforming it into a clue to the understanding of fundamental problems is brought out strikingly in his work leading to the discovery of the Raman effect itself.

Raman is a born experimental physicist, and has been guided by the conviction that real progress in physics can be achieved by the application of considerations based on experience and reason to experimental observations of properly chosen phenomena. He has advanced directly and successfully along this straight path without often branching into mathematical physics. Yet whenever occasion arose he has shown that he possessed the mathematical equipment essential to the interpretation of his work. He has also recognised and acknowledged the fundamental importance of ideas of a mathematical or deductive nature. Thus, in the realm of his researches in crystal physics, he has realised the importance of group theory, and the theory of group representations, and encouraged investigations based on such theoretical considerations. He has also shown facility in choosing the right type of mathematical technique needed in his work, and an uncanny faculty for seeing clearly through a mass of complicated mathematical calculations. His theory of the diffraction of light by high frequency sound waves is a striking example of this. Like all great physicists, however, he has placed facts first, and hypothesis always second.

Though the work of Raman and his school has lain in apparently diverse fields it is easy to discern a coherence and unity in them. The central and guiding theme of all his physical research has been optics in all its aspects. His special love has been for crystal physics, and in particular, physics of the diamond, in which subject he is a recognised authority. He has recently struck new paths in crystal physics, and introduced new concepts regarding crystal structure.

Another noticeable characteristic of Raman's scientific work is its sturdy individualism which is a consequence of the fact that when he started his career he belonged to no particular school of physics, but had to build one himself. He is thus a true pioneer who has had the vision and courage successfully to explore unknown lands in physics. This circumstance has made him attach great importance to an independent approach to problems, and if his valuable example of striking out new and independent paths of research were to infect other scientific workers in our country, we are assured of a bright scientific future indeed. Further, the fact that he had to start work as an independent investigator without the facilities of an already well-equipped laboratory has brought out to the full his skill as an experimenter. Most of his experiments have required neither costly machinery nor any type of special techniques, but have been so simply devised as to be easily understood even by a layman. In fact, the apparatus with which he demonstrated the Raman effect is a model of simplicity and by no means a costly one, but nevertheless this simple experiment is one of the important milestones in the world's knowledge of nature.

It is perhaps not very well known that Raman has shown a fine æsthetic outlook in his research work. His choice of topics for investigation, and his way of handling them bring out clearly his innate artistic nature. His love of music, colour, light, vibration, symmetry, harmony, pattern, structure, and architecture is but the result of a deep appreciation of the beautiful in nature. His researches on musical instruments, numerous beautiful phenomena of wave optics, the colour of the sea, colour in the plumage of birds, iridiscent shells and mother-of-pearl, vibration in crystals, and above all his studies on the form, symmetry and structure of diamond based on fluorescence, phosphorescence and birefringence patterns are a few examples of his æsthetic tastes in research. He has one of the finest private scientific collections of diamonds and other beautiful crystals, and loves them as only a true artist can.

None who has come in contact with Raman can have failed to notice his very wide and catholic interest in many branches of science besides physics. He has perhaps done as much for chemistry as for physics. His interest in geology based on deep knowledge, specially in the fields of mineralogy and crystallography, has been a stimulant for the geological research of many workers in India. Some aspects of plant life, and animal life, specially birds, have always had a deep fascination for him. He has shown keen interest in and appreciation of astronomical and astrophysical research, both observational and theoretical. Indicative of his wide interests are his plans to build an astronomical observatory, a biological research unit, and a mineralogical laboratory in the new Raman Research Institute. In spite of criticism from some quarters, it can be confidently said that by his collaboration and encouragement he has given the necessary incentive to studies in mathematics even of the purest type. It is safe to say that there is no branch of science in which he has not encouraged creative and original work, and this augurs well for the development of fundamental research in the country in its new set-up.

Raman is not only a great investigator but also a great teacher in the true sense of the word. His ideas and personality have attracted many young research students, and he has held their loyalty and affection by extending a never-failing friendship to them. He has not only taught methods of physical research to his students, but by his own shining example made them realise the necessity of endurance, steadiness and hard work in the pursuit of knowledge. While giving help and encouragement in plenty, he has always expected and sometimes demanded from his students the best that they could give. The writer of this article has had many occasions to see the great care with which he would supervise the papers of his students, sometimes going to the extent of re-writing whole sections. No paper ever leaves his laboratory until he is completely satisfied with it.

The feelings of respect and admiration which his students have towards him can be ascribed to his fairness and even generosity in acknowledging a pupil's ideas or originality. He is very liberal minded and gives away whole lines of research which lesser men would be tempted to keep for themselves. Whenever he discovers any originality in a pupil he will do all he can to develop it. His simplicity and informality are best seen in his discussions with students. Some penetrating remark made by him at such discussions has been the starting point, as some of his pupils have confessed, of a complete line of investigation undertaken by them later. This has been true not merely in his own special field of research, but in other subjects as well.

Raman has rendered signal service to scientific advance in India as much by his contributions to knowledge as by his training of students in methods of research. He has exerted a profound influence on the work and outlook of not only his students but most of his contemporaries.

Unlike many scientific investigators who are giants in their own laboratories but dwarfs outside unable to take a due share in the national life of their country, Raman has fully participated in several walks of national activity, and is eager to serve the cause of scientific and technological advance in India. Possessing in a rare measure the extraordinary gift of making the most difficult problems in physics appear simple, and with a keen and irresistible sense of humour, he has admirably filled the role of an eminent popular lecturer on scientific subjects. Popularisation of science in the country owes not a little to his gifts of eloquence and exposition.

To have accomplished so much in one's own chosen field of research might have contented many men, but it is not enough for Raman. He has an unquenchable thirst for knowledge, and great energy for exploration, and for him " 'Tis not too late to seek a newer world ". On this occasion of his Sixtieth Birthday, we heartily wish him many more happy returns of the same with the hope that his vision and wisdom may well and truly serve the cause of science.

B. S. MADHAVA RAO.

SIR C. V. RAMAN AND CRYSTAL PHYSICS

OPTICAL theory and the physics of crystals are linked together almost inseparably in the history of their development. It is not surprising, therefore, that his love of optics has led Sir C. V. Raman to take an ever-increasing interest in crystal physics, as will be evident from the titles of the papers communicated by him to the Academy during the past decade or two. Many aspects of the subject have received his attention at some time or another. More recently, also, he has considered the fundamental problems of crystal physics from a standpoint which, while it is essentially novel, has proved highly successful in explaining the facts of observation. In these circumstances, it has appeared desirable to include in the present Symposium on Crystal Physics which commemorates his Sixtieth Birthday, a classified list of the papers on the subject which have emerged from his laboratories during the last thirty years. It is of particular interest to trace the development of his ideas and to indicate the fundamental character of the contributions made by him and his school. This will be done in the present survey.

Some of the most beautiful illustrations of optical principles are to be found in the phenomena of crystal optics. Haidinger's and Quetelet's rings in crystalline plates, the iridescence of twinned crystals of potassium chlorate, the optical effects observed with amethystine quartz, the diffraction of light by the laminar boundaries in mica and the haloes observed in the Christiansen experiment with crystal powders are amongst the subjects of this kind investigated during the earliest years of Raman's professoriate by his pupils. The phenomena of conical refraction exhibited by biaxial crystals have also had a special fascination for him. Amongst the discoveries made in this field may be mentioned that of the formation of sharply focussed optical images by plane plates of biaxial crystals. That naphthalene crystals have an extremely large angle of conical refraction and exhibit the effects arising therefrom in a very striking way is another significant contribution. Many studies have also been published of the beautiful phenomena exhibited by the nacreous layer in molluscan shells and the manner in which they are influenced by the size, shape and relative orientation of the platelets of aragonite appearing in its stratifications.

2. THE SCATTERING OF LIGHT IN CRYSTALS

In the latter part of 1921, Raman commenced his studies on the diffusion of light in transparent media. These were systematically pursued over a period of years until finally they led to the discovery of the effect known by his name. The work of this epoch was of significance for crystal physics in several ways. The first major contribution which emerged at an early stage was the discovery of the phenomenon of the *thermal diffusion of light in crystals.* Raman was led to recognize its existence by the fact that the clearest crystals available to him, *viz.*, a polished sphere of quartz and a large transparent block of ice, both exhibited a blue opalescence when traversed by a concentrated beam of sunlight and that the intensities observed were of the right order of magnitude, both relatively and absolutely. Ice, which has a high compressibility, showed the phenomenon more conspicuously than quartz, in spite of the higher refractive index of the latter. The inference suggested by these facts, *viz.*, that the scattering had its origin in the fluctuations of optical density in the crystal due to the thermal agitation was confirmed by heating a quartz block. The intensity of the opalescence was then found to increase, as was to be expected.

Following these early observations, the work with crystals was laid aside and studies with gases and liquids were energetically pursued, as they offered a larger variety of promising material for quantitative work. In February 1928, Raman switched over from sunlight to the monochromatic radiations provided by the mercury arc for his studies on light scattering. When his pocket spectroscope revealed clearly the appearance of radiations of altered frequency in the light scattered by liquids, he instantly realised the importance of looking for a similar phenomenon in the light scattered by crystals as well as by amorphous solids. Observations with a large block of crystalline ice showed sharp displaced lines in approximately the same positions as those observed with distilled water. This fact and its theoretical significance are clearly brought out in the paper announcing the discovery of the effect. The magnitude of the frequency shifts observed with ice showed that the phenomenon was of a different nature from the thermal diffusion of light in crystals discovered in 1921, and was to be accounted for on the same basis as the corresponding effect observed with water, *viz.*, an exchange of energy between the incident light quanta and the vibrations of the structural units of the substance.

3. Birefringence and Pleochroism in Crystals

Apart from the discovery of the Raman effect, the studies on the scattering of light in gases and liquids carried on during the years 1921 to 1927 opened up several other pathways of research. They threw a vivid light on the nature of the liquid state, showing clearly that it is far from being a random distribution in space of the molecules composing it. This led Raman to seek a confirmation of his ideas by undertaking with the aid of his collaborators a series of systematic studies on the X-ray diffraction haloes of liquids and glasses. The results obtained in these studies were found to be explicable on the same basis as the facts observed earlier in light-scattering. Of special significance to crystal physics were the determinations of the optical anisotropy of the molecules or ions made possible by measurements of the intensity and depolarisation of light-scattering in fluids. A correlation became evident between the optical anisotropy of molecules in fluids and the birefringence exhibited by the same substances in the crystalline state. This indicated that the birefringence of crystals is determined principally by the optical anisotropy of the molecules or ions and by the manner in which they are orientated with respect to the crystal axes. Thus, from the known optical anisotropy and the observed features of the birefringence, it becomes possible to draw useful conclusions regarding the structure of the crystal. Indications of this kind were found to be particularly useful in cases where the optical anisotropy and the birefringence are both large, *e.g.*, organic crystals of the aromatic class.

The extensive data obtained regarding optical anisotropy also enabled some general conclusions to be drawn regarding the relation between this property and the chemical constitution of the molecule. It emerged that a large optical anisotropy is accompanied by the presence of absorption in the near ultra-violet or visible region of the spectrum. Further, in such cases, the crystals of the substance exhibit a marked pleochroism in which the axis of maximum absorption coincides with that of the largest optical polarisability, though there are some exceptions to this rule.

4. MAGNETIC ANISOTROPY OF CRYSTALS

Many papers on magnetism and magneto-optics figure in the published output of Raman's school. The early studies on light-scattering, remarkably enough, gave an impetus to work in this field. Magnetic birefringence in liquids owes its origin to the fact that while the magnetic field tends to orientate the molecules, their optical anisotropy results in double refraction. Thus, simultaneous studies on magnetic double refraction and on light-scattering in liquids enable the magnetic anisotropy of the molecules or ions to be evaluated and connected with the magnetic anisotropy of the solid crystal of the same substance. The known magnetic behaviour of the crystalline nitrates and carbonates was successfully explained by Raman and Krishnan in this way. The large magnetic anisotropy of the benzene ring deduced by them in the same fashion proved to be a fundamental discovery, since it led to the recognition of the still larger anisotropy of other aromatic molecules and opened the way to the interpretation of the magnetic behaviour of crystals of those substances. Indeed, magnetic studies were shown to be a powerful aid to crystal structure analysis by the early work of Bhagavantam with naphthalene and anthracene. So impressed was Raman by the importance of the method that he initiated studies on magnetic birefringence in many liquids in which it had not been previously observed. This work led to the discovery of the weak negative birefringence exhibited by water, the aliphatic hydrocarbons and other liquids. Crystals of substances exhibiting such negative magnetic birefringence show a relation between their magnetic and optical behaviour quite different from that of crystals of substances, *e.g.*, the aromatic series, which show a positive magnetic birefringence in the liquid state.

5. RAMAN EFFECT STUDIES

Raman's discovery of 1928 opened up a vast new field of activity which was naturally taken up by his collaborators with enthusiasm, and many publications dealing with different aspects of the subject emerged from his laboratory. The effect exhibited by crystals was in the foreground of this activity from the beginning in view of its evident importance for an understanding of the theory of solids; indeed, during the last ten years, work with gases and liquids has been completely laid aside in favour of crystals which present both a challenge and an incentive to investigators in the field. They are a challenge since the difficulties of obtaining satisfactory material and of eliminating spurious effects due to parasitic illumination and instrumental defects are great. They are an incentive, since the sharpness of the Raman lines observed with crystals encourages employment of the most powerful instruments capable of revealing the maximum of detail and yielding data with the precision characteristic of spectroscopy. The major aim of the work in recent years has been that of elucidating the physical problems of the solid state, the substances chosen and the studies undertaken being both determined by this aim. Amongst the topics investigated are the following: the influence of temperature on the sharpness, position and intensity of the lines; the changes in the spectra accompanying thermal transitions in the crystal; the change from the solid to the liquid state; the identification of the modes of vibration active in light-scattering; the influence of crystal symmetry and structure on the spectra, and so forth. We cannot here describe either the techniques employed or the results obtained in these researches. It is necessary, however, to mention an important group of investigations designed to elucidate the fundamental problem of the nature of the vibration spectrum of a crystal. Taking for instance, the case of diamond, its Raman spectrum as ordinarily recorded is a single extremely sharp line with a frequency shift of 1332 cm.$^{-1}$ Obviously, this cannot represent the complete vibration spectrum and there should be other frequencies in it. The task of establishing their existence has been successfully accomplished by the present writer and the results are of very great interest. The results show in a perfectly unambiguous way that the vibration spectrum of diamond consists of a whole series of sharply defined discrete frequencies, of which only the highest is represented by the frequency shift of 1332 cm.$^{-1}$ The remaining frequencies do not appear in the first-order Raman spectrum ordinarily recorded. But with adequate exposures they appear as overtones and combinations in the so-called second-order Raman spectrum. The latter has also been successfully recorded with numerous crystals besides diamond.

6. THE THERMAL SCATTERING OF LIGHT

We return to the phenomenon discovered by Raman in 1921, namely the thermal diffusion of light in crystals. The thermal agitation which gives rise to it may be identified with stationary elastic vibrations of various modes and frequencies determined by the elastic constants and by the size and shape of the crystal. The diffusion itself would arise from the modulation of the optical wave-motion by the elastic vibrations and should therefore exhibit frequency shifts, while its strength would be determined by the photoelastic properties of the crystal. It would evidently not be easy to determine the distribution of intensity in the resulting spectrum unless, following L. Brillouin, we regard the crystal as of infinite extension. Whether this is always permissible is a question.

The frequency shifts to be expected theoretically are small and therefore not easily determined; lack of perfect monochromatism in the incident radiation and any Tyndall scattering present give rise to serious experimental difficulties. The subject is, nevertheless, of great interest and many studies have been published. Particular success has been achieved in the case of diamond which gives large frequency shifts not requiring interferometric aid for their observation. A perfect elimination of the Tyndall scattering is also possible by the use of the resonance radiation of mercury and a mercury vapour filter. An experimental result of great importance which has been established with this technique is that the elastic vibrations in a crystal are wholly incapable of giving rise to an observable diffusion of light, unless their "wave-lengths" are such as to give a regular Brillouin reflection. The behaviour of the elastic vibrations in the crystal is thus in complete contrast with that of the modes of vibration with discrete frequencies which readily record themselves in the second-order Raman spectrum even when they do not appear in the first order.

7. THE VIBRATION SPECTRA OF CRYSTALS

A fundamental question in the theory of the solid state is the nature of the vibration spectrum of a crystal. The new approach to the solution of this problem made by Raman is based on the idea that since we are concerned with the vibrations of a mechanical system, we have necessarily to consider its "normal modes". Further, the approach to the problem of finding these modes is necessarily different for the "elastic" vibrations in a continuum, and the "atomic" vibrations in a discrete structure. In the former case the vibrational modes and frequencies are determined by the external boundary conditions, while in the latter case, the time-periodic movements in the units of the structure are analogous to the vibrations of a polyatomic molecule and hence the external boundary conditions are wholly irrelevant. Following up this idea in a straightforward way, Raman derived his fundamental proposition that the structure of a crystal having p atoms in each of the cells of its structure has $(24p-3)$ normal modes of vibration, and the same number of discrete frequencies of vibration unless this is reduced by reason of symmetry of the crystal and consequent degeneracy of the modes. This is a result of far-reaching importance which explains in a completely quantitative fashion the experimental results mentioned in the preceding two sections. In particular, the experimental fact that the 'elastic vibrations' of a crystal are wholly inactive in light-scattering (except in the case of a Brillouin reflection), while the structural vibrations are active in the second-order if they are not active in the first-order is a clear indication that they are different in their physical nature. The recognition of such a difference is, in fact, the starting point of the new theoretical approach.

8. THE STRUCTURE AND PROPERTIES OF DIAMOND

Diamond is a substance of extraordinary interest to the physicist engaged in the study of crystals, since it exhibits the characteristic properties of the solid state in an exceptional degree. For this reason the investigation of the physical behaviour of diamond has of recent years formed one of the principal activities of Raman's laboratory and many papers have been published describing the results.

The properties of diamond may be broadly divided into two groups. The first group comprises those that do not exhibit significant variations as between different specimens of diamond. This group includes density, hardness, elasticity, thermal expansion, specific heat, thermal conductivity, refractivity, dispersion, photoelasticity, dielectric constant, magnetic susceptibility, Faraday effect, Raman effect, and infra-red absorption of the second and higher orders. The second group of properties are those which exhibit variations, often of a most striking character, as between different diamonds. Amongst them may be listed infra-red absorption of the first order, absorption spectra in the visible and ultra-violet regions, fluorescence excited by visible and ultra-violet light and by X-rays, phosphorescence, photoconductivity, optical birefringence, intensity and sharpness of the Laue and Bragg X-ray reflections, and dynamic X-ray reflections. If the variations in the properties listed above had been unrelated to each other, the study of the diamond would indeed have been a very perplexing subject. Happily, this is not so, as has been shown by Raman and his collaborators by studies covering all the properties listed above with an extensive collection of material. The results present such striking correlations between the variations of the different properties as to leave no room for doubt that differences are systematic and arise from fundamental differences in crystal structure. This inference receives direct observational support from studies on the crystal morphology of diamond. The situation may be summed up broadly by the statement that the electronic structure of diamond may possess either tetrahedral or octahedral symmetry. Assuming each atom of carbon to possess only tetrahedral symmetry, geometric considerations indicate that there must be two sub-species (positive and negative, respectively) of the tetrahedral type and two sub-species of the octahedral type. The recognition of the existence of these four species of the diamond structure, appearing separately or together in any actual specimen of diamond enables the varied behaviours actually met with to be satisfactorily described and interpreted.

9. LUMINESCENCE AND ABSORPTION SPECTRA

The luminescence of diamond, a long-known but neglected phenomenon, has been studied with great thoroughness by Raman and his collaborators with results of exceptional interest. Two distinct types of luminescence based on different electronic transitions are observed, and the same electronic transitions can also appear in absorption. They may be coupled with vibrational transitions in the crystal lattice and as the result, the principal emission or absorption in each case appears accompanied by subsidiary radiations of less and greater frequency respectively. The emission and absorption spectra exhibit mirror-image symmetry with respect to each other about the electronic frequency. The lattice frequencies deduced from the spectra agree with those given by the new crystal dynamics, which was in fact first developed to explain the effects observed in the luminescence spectrum of diamond.

The coupling of electronic with vibrational transitions so clearly manifested in the case of diamond is a general feature in the luminescence spectra of crystals. As a consequence, Raman effect studies are of great assistance in interpreting such spectra. As an illustration, one may cite the case of the fluorescence and absorption of the uranyl salts, as also the cases of alumina and of topaz investigated by the present writer. The lattice frequencies of magnesium oxide calculated on the basis of theory fit very well with those deduced from its luminescence spectra resulting from the presence of a trace of chromic oxide as impurity.

10. INFRA-RED ABSORPTION SPECTRA

All diamonds without exception exhibit an infra-red absorption spectrum of the second order, while the diamonds of the tetrahedral class exhibit also a first order absorption. These spectra have been thoroughly investigated and are explicable in all their details on the basis of the new lattice dynamics. Particularly interesting is the fact that the two weakest second-order Raman lines (2176 cm.$^{-1}$ and 2015 cm.$^{-1}$) are represented in the second-order infra-red absorption by its two most conspicuous peaks, as is to be theoretically expected. A feature which manifests itself conspicuously in the first order infra-red absorption by diamond is that all the nine fundamental modes of vibration of the lattice are active, though in different degrees, and not merely the so-called principal oscillation having the highest frequency. The absorption curves exhibit distinct peaks corresponding to the different modes, but their resolution is far from perfect. These features are explicable as due to the coupling of the different modes with each other due to anharmonicity. Such coupling would necessarily manifest itself even more strongly in the case of strongly infra-red active crystals and offers a basis for an explanation of the features exhibited by their absorption spectra.

11. THERMO-OPTIC PROPERTIES OF CRYSTALS

Studies of the effect of temperature on the optical properties of diamond have pointed the way to the development of a successful quantitative theory of the thermo-optic behaviour of crystals. The refractive index of diamond increases instead of diminishing with rise of temperature, this increase becoming more rapid as we approach the violet end of the spectrum. In consequence, the dispersion of diamond is enhanced by rise of temperature even more rapidly than its refractive index. The sharply defined electronic absorption lines in the visible and ultra-violet region exhibited by diamond at low temperatures are observed to drift towards lower frequencies when the temperature is raised. It may therefore be reasonably assumed that the characteristic frequency in the extreme ultra-violet principally responsible for the dispersion also shifts downwards with rise of temperature. Such a shift would result in an increase of dispersion and refraction which would only be partially be set off by the diminution caused by the thermal expansion. Not only does this idea work successfully in the case of diamond, but it is found to be remarkably successful also in explaining the facts observed with numerous other crystals, both those which are isotropic, *e.g.*, the alkali halides and those which are birefringent, *viz.*, quartz, calcite and aragonite. The basis of the theory, namely the diminution of the characteristic frequencies in the remote ultra-violet with temperature, also finds direct observational support.

12. PHOTOELASTIC PROPERTIES OF CRYSTALS

One of the earliest attempts to develop a quantitative theory of the photoelastic behaviour of crystals was that made at Raman's suggestion in 1927 by Kedareswar Banerji. The subject has acquired considerable importance in recent years by reason of its relationship to other phenomena, *viz.*, the optical effects arising from mechanical oscillations in a crystal and the thermal diffusion of light. The theory of the diffraction of light in ultrasonic fields originally put forward by Raman and Nath to explain the effects observed in liquids, applies *mutatis mutandis* to the case of a crystal when the relevant piezo-optic constants are introduced in the formulæ. The recent determination of the piezo-optic constants of diamond was, in fact, made with a view to work out the consequences of Brillouin's theory of the thermal scattering of light in it. Measurements with other crystals will no doubt prove of great value in this field of research.

13. MAGNETO-OPTIC BEHAVIOUR OF CRYSTALS

One of the many remarkable properties of diamond is the feebleness of the Faraday effect observed with it when considered in relation to its high dispersive power. The rotation of the plane of polarisation of light produced by a magnetic field is only one-fourth of that to be expected on the basis of the well-known Becquerel formula. The measurements which revealed this fact were made possible by the plates of diamond free from birefringence included in Raman's collection. The explanation for the low value is evidently to be found in the covalent character of the bonding of the atoms of carbon in the crystal with each other. The case of diamond thus clearly indicates that measurement of the "magneto-optic anomaly" exhibited by a crystal offers a method of ascertaining the nature of the electronic states in its atoms or ions. Studies with other crystals have since been pursued with this aim in view.

14. ELASTIC PROPERTIES OF CRYSTALS

Methods based on the use of piezo-electrically excited oscillations have opened out new possibilities for the accurate determination of the elastic constants of crystals. The recent work of Bhagavantam and his collaborators at Waltair may be specially mentioned in this connection. The problem naturally arises of seeking to connect these experimentally observed constants with the known crystal structure and if possible to derive them theoretically on the basis of that structure. The first step in any such attempt is evidently the evaluation of the interàtomic forces arising from the displacements of the atoms from their positions of equilibrium. One way of finding these forces is to connect them with the frequencies of atomic vibration made accessible to observation by the Raman effect and from these frequencies as actually observed to evaluate the forces. A rigorous method of accomplishing this has been worked out in the case of various crystals. Difficulties arise in the next step, namely that of evaluating the elastic constants from the interatomic forces, but we shall not discuss them here.

15. THE THERMAL PROPERTIES OF CRYSTALS

The evaluation of the specific heat of a crystal requires a knowledge of its vibration spectrum. The proposition that this spectrum consists of $(24p-3)$ discrete frequencies places the theory of specific heats on a very simple and intelligible basis. Further, when these frequencies are accessible to direct spectroscopic observation, a comparison between the actual and calculated specific heats becomes possible. It may be remarked that the three excluded degrees of freedom represent the spectrum of elastic vibrations in the crystal. These appear at the very lowest end of the frequency range. Hence in most cases it is a sufficient approximation to regard them as fully excited at the temperature of observation and make the necessary addition to the specific heat; a more exact calculation may, however, be necessary if p be small and if the temperature is very low. Calculations of the specific heat made in this manner for crystals for which the necessary spectroscopic data are available, *e.g.*, diamond, show a satisfactory agreement with the facts.

Another property of a crystal which is intimately related to its vibration spectrum is its thermal expansion. Data regarding the thermal expansion coefficient of crystals are rather meagre. For example, no data were available for diamond above the room temperature. The present writer has developed a new precision method of measuring the coefficient of thermal expansion of crystals and applied it to the case of diamond which, as is well known, has a very small dilatation. Attempts to evaluate the thermal expansion of diamond and of other crystals theoretically on the basis of the spectroscopic data as in the case of their specific heats have given very encouraging results.

16. X-RAY STUDIES

The striking developments in X-ray physics which followed in the wake of Laue's great discovery of 1912 were already accomplished facts when Raman commenced his professoriate. Hence, neither X-ray spectroscopy nor crystal structure analysis was ever adopted by him as a part of his regular research programme. Nevertheless, these subjects have interested him greatly, as will be evident from the numerous X-ray studies published from time to time from his laboratory.

In April 1940, Raman and Nilakantan published in an article in *Current Science* under the title "A new X-ray effect", some strongly exposed Laue photographs obtained with an octahedral cleavage plate of diamond and the X-radiation from a copper target. These photographs showed some remarkable features which they explained as arising from dynamic reflections of the incident X-radiation by the (111) planes of the crystal. They gave reasons for believing that the crystal planes giving these reflections were set in vibration with the same frequency as that observed in the Raman spectrum of diamond and that the excitation was quantum-mechanical as in the case of the Raman effect. The reality of the effect is indisputable and on the basis of the explanation indicated, it is clearly of fundamental importance. Raman and Nilakantan subsequently published further experimental results which confirmed the correctness of the explanation given by them. We shall not here enter further into the subject except to remark that the explanation of this X-ray effect stands in the closest relation to the problem of the nature of the vibration spectrum of a crystal. The same question also enters fundamentally into the theory of the diffraction of X-rays by crystals and of the influence of temperature on the same.

R. S. KRISHNAN.

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2.	Birefringence	6
3.	Magnetic and magneto-optic properties	30
4	Photo-elasticity and thermo-optic behaviour	11
5.	Thermal agitation, scattering of light and hypersonics	11
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12.	Crystal structure studies	15
13.	Structure and properties of diamond	31
14.	Miscellaneous	8
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24	Phenomena of conical refraction ..	C. V. Raman	*Curr. Sci.*	1942, **11**, 44
25	Optical images formed by conical refraction	C. V. Raman and T. M. K. Nedungadi	*Nature*	1942, **149**, 552

2. BIREFRINGENCE

1	The birefringence of crystalline carbonates, nitrates and sulphates	C. V. Raman	*Nature*	1926, **118**, 264
2	Colour and optical anisotropy of organic compounds	Do.	*Ibid.*	1929, **123**, 494
3	Relation between colour and molecular structure	C. V. Raman and S. Bhagavantam	*Ind. Jour. Phys.*	1929, **4**, 57
4	Optical properties of some aromatic crystals	K. L. Narasimhan	*Ibid.*	1931, **6**, 233
5	The dispersion, birefringence and optical activity of quartz	T. Radhakrishnan	*Proc. Ind. Acad. Sci.*	1947, **25**, 260
6	The dispersion formulæ of the alkali halides	Do.	*Ibid.*	1948, **27**, 165

3. MAGNETIC AND MAGNETO-OPTIC PROPERTIES

1	The magneto-crystalline properties of the Indian braunites	K. Seshagiri Rao	*Proc. Ind. Assoc. Cult. Sci.*	1920, **6**, 87
2	The magnetic anisotropy of crystalline nitrates and carbonates	K. S. Krishnan and C. V. Raman	*Proc. Roy. Soc.*	1927, **115**, 549

No.	Subject	Author	Journal	Year
3	Diamagnetism and crystal structure	C. V. Raman	*Nature*	1929, **123**, 945
4	Magnetic behaviour of organic crystals	Do.	*Ibid.*	1929, **123**, 605
5	Anomalous diamagnetism	Do.	*Ibid.*	1929, **124**, 412
6	Magnetic birefringence in solutions and its relation to crystal structure and properties	M. Ramanadham	*Ind. Jour. Phys.*	1929, **4**, 109
7	The magnetic anisotropy in naphthalene crystals	S. Bhagavantam	*Proc. Roy. Soc.*	1929, 124, 545
8	The magnetic and optical properties of benzene ring in aromatic compounds	Do.	*Ibid.*	1929, **126**, 143
9	Anomalous diamagnetism of graphite	S. Paramasivan	*Ind. Jour. Phys.*	1929, **4**, 139
10	Magnetic behaviour of some organic crystals	S. Bhagavantam	*Ibid.*	1929, **4**, 1
11	Diamagnetism and molecular structure	C. V. Raman	*Proc. Phy. Soc., London*	1930, **42**, 309
12	Anomalous diamagnetism and crystal structure	V. I. Vaidyanathan	*Ind. Jour. Phys.*	1930, 5, 559
13	Orientation of the molecules in naphthalene and anthracene crystals	K. Banerji	*Ibid.*	1930, **4**, 557
14	The magnetic anisotropy of naturally occurring substances. Part I. Mother of pearl	P. Nilakantan	*Proc. Ind. Acad. Sci.*	1935, 2, 621
15	The magnetic anisotropy of naturally occurring substances. Part II. Molluscan shells	Do.	*Ibid.*	1936, 4, 542
16	Magnetic anisotropy of rhombic sulphur	Do.	*Ibid.*	1936, **4**, 419
17	Temperature variation of the magnetic anisotropy of ammonium nitrate	Do.	*Phys. Rev.*	1937, **52**, 383
18	Temperature variation of magnetic anisotropy of organic crystals	Do.	*Nature*	1937, **140**, 29
19	Magnetic anisotropy of naturally occurring substances. Part III. Wood lignin and wood cellulose	Do.	*Proc. Ind. Acad. Sci.*	1938, 7, 38
20	Magnetic anisotropy and pleochroism of biotite mica	Do.	*Ibid.*	1938, **8**, 39
21	Studies in crystal magnetism	Do.	*Jr. Ind. Inst. Sci.*	1940, **23**, 187
22	Magnetic susceptibility of diamond	A. Sigamony	*Proc. Ind. Acad. Sci.*	1944, **19**, 310

23	Magnetic susceptibility and anisotropy in carborundum	Do.	*Ibid.*	1944, **19**, 377
24	The magnetic properties of tourmaline and epidote	Do.	*Ibid.*	1944, **20**, 200
25	The magnetic behaviour of iron pyrites ..	Do.	*Ibid.*	1944, **20**, 204
26	The magnetic properties of augite ..	Do.	*Ibid.*	1944, **20**, 261
27	The magnetic behaviour of tektite ..	Do.	*Ibid.*	1944, **20**, 15
28	The Faraday effect in diamond	S. Ramaseshan	*Ibid.*	1946, **24**, 104
29	The magnetic properties of iron pyrites ..	Do.	*Ibid.*	1947, **25**, 201
30	Faraday effect in some cubic crystals ..	Do.	*Ibid.*	1947, **25**, 459

4. PHOTO-ELASTICITY AND THERMO-OPTIC BEHAVIOUR

1	Theory of photoelasticity	K. Banerji	*Ind. Jour. Phys.*	1927, **2**, 195
2	Photo-elastic constants of diamond ..	G. N. Ramachandran	*Proc. Ind. Acad. Sci.*	1947, **25**, 208
3	Thermo-optic behaviour of solids. I. Diamond	Do.	*Ibid.*	1947, **25**, 266
4	Thermo-optic behaviour of solids. II. Fused quartz	Do.	*Ibid.*	1947, **25**, 280
5	Thermo-optic behaviour of solids. III. Fluorspar	Do.	*Ibid.*	1947, **25**, 286
6	Thermo-optic behaviour of solids. IV. Zinc blende	Do.	*Ibid.*	1947, **25**, 375
7	Thermo-optic behaviour of solids. V. Alkali halides	Do.	*Ibid.*	1947, **25**, 481
8	Birefringence of crystals and its temperature variations. Part I. Calcite and Aragonite	Do.	*Ibid.*	1947, **26**, 77
9	Birefringence of crystals and its temperature variations. Part II. Sodium and potassium nitrates	Do.	*Ibid.*	1947, **26**, 114
10	Temperature variation of the refractive indices of quartz	T. Radhakrishnan	*Ibid.*	1947, **25**, 382
11	Temperature variation of the refractive indices of quartz	Do.	*Ibid.*	1948, **27**, 44

5. THERMAL AGITATION, SCATTERING OF LIGHT AND HYPERSONICS

No.	Subject	Author	Journal	Year
1	The molecular scattering of light by liquids and solids	C. V. Raman	*Nature*	1921, **108**, 402
2	Smoky quartz	Do.	*Ibid.*	1921, **108**, 81
3	Optical observations of the thermal agitation of the atoms in crystals	Do.	*Ibid.*	1922, **109**, 42
4	Molecular diffraction of light	Do.	Calcutta University Press	1922
5	Thermal opalescence in crystals and colour of ice in glaciers	Do.	*Nature*	1923, **111**, 13
6	The scattering of light by smoky quartz	N. K. Sur	*Proc. Ind. Assn. Cult. Sci.*	1923, **8**, 271
7	Doppler effect in light scattering	C. V. Raman	*Nature*	1931, **128**, 636
8	Optical observation of the Debye heat waves in crystals	C. V. Raman and C. S. Venkateswaran	*Ibid.*	1938, **142**, 250
9	The scattering of light in quartz	V. Chandrasekharan	*Proc. Ind. Acad. Sci.*	1947, **25**, 256
10	The scattering of polarised light beams in birefringent solids	Do.	*Ibid.*	1947, **26**, 110
11	Thermal scattering of light by diamond	R. S. Krishnan	*Nature*	1947, **159**, 740

6. RAMAN SPECTRA

No.	Subject	Author	Journal	Year
1	A new radiation	C. V. Raman	*Ind. Jour. Phys.*	1928, **2**, 387
2	The Raman effect in crystals	I. Ramakrishna Rao	*Ibid.*	1928, **3**, 123
3	The Raman effect in crystals	K. S. Krishnan	*Nature*	1928, **122**, 477
4	Relation of Raman effect to crystal structure and properties of diamond	S. Bhagavantam	*Ind. Jour. Phys.*	1930, **5**, 169
5	Further studies on the Raman effect of diamond	Do.	*Ibid.*	1930, **5**, 573
6	Raman spectra of crystalline inorganic chlorides	P. Krishnamurthi	*Ibid.*	1930, **5**, 113
7	Raman spectra of inorganic crystals. Part II. Hydroxides, cyanides and sulphocyanides	Do.	*Ibid.*	1930, **5**, 651

8	Raman spectra of crystalline powders ..	Do.	*Nature*	1930, **125**, 463
9	Raman effect, fluorescence and colour of diamonds	S. Bhagavantam	*Ibid.*	1930, **126**, 168
10	Raman spectra of inorganic crystals. Part I. Substances containing XO_3 and XO_4 groups	P. Krishnamurthi	*Ind. Jour. Phys.*	1930, **5**, 633
11	Raman effect in paramagnetic crystals ..	Do.	*Nature*	1930, **126**, 169
12	Raman effect in some crystalline inorganic sulphates; influence of paramagnetism on Raman lines	Do.	*Ind. Jour. Phys.*	1930, **5**, 183
13	Raman effect in metallic halides ..	Do.	*Nature*	1930, **125**, 892
14	Raman spectrum and infra-red absorption of sulphur	Do.	*Ind. Jour. Phys.*	1930, **5**, 105
15	The Raman effect in crystal powders of inorganic nitrates	Do.	*Ibid.*	1930, **5**, 1
16	Raman effect in calcite and aragonite ..	S. Bhagavantam	*Zeit. fur. Krist.*	1931, **77**, 43
17	Raman spectra of some organic crystals and solutions	P. Krishnamurthi	*Ind. Jour. Phys.*	1931, **6**, 309
18	Raman spectra of organic sulphides ..	S. Venkateswaran	*Ibid.*	1931, **6**, 51
19	Raman spectra of inorganic crystals—Part III	P. Krishnamurthi	*Ibid.*	1931, **6**, 7
20	Raman spectra of pinene, thiophene, salol and thymol	S. Venkateswaran and S. Bhagavantam	*Ibid.*	1932, **7**, 585
21	Raman spectra of some metallic halides ..	C. S. Venkateswaran	*Proc. Ind. Acad. Sci.*	1934, **1**, 850
22	Raman spectra of sulphur in solid and liquid states	Do.	*Ibid.*	1934, **1**, 120
23	The Raman spectra of iodic acid and alkaline iodates as solids and as solutions	Do.	*Ibid.*	1935, **2**, 119
24	Raman spectrum of phosphorus ..	Do.	*Ibid.*	1935, **2**, 260
25	Raman spectra of metallic formates and constitution of formic acid	Do.	*Curr. Sci.*	1935, **4**, 736
26	Raman spectra of metallic formates and constitution of formic acid	Do.	*Proc. Ind. Acad. Sci.*	1935, **2**, 615
27	The Raman spectrum of crystalline selenious acid	Do.	*Curr. Sci.*	1936, **4**, 309
28	Raman spectra of selenious acid and its sodium salts	Do.	*Proc. Ind. Acad. Sci.*	1936, **3**, 533

No.	Subject	Author	Journal	Year
29	Raman spectra of sulphur and phosphorus. Part I. Polarisation and molecular structure	C. S. Venkateswaran	*Proc. Ind. Acad. Sci.*	1936, **4**, 345
30	Raman spectra of sulphur and phosphorus. Part II. Lattice oscillations	Do.	*Ibid.*	1936, **4**, 414
31	Raman spectra of orthophosphoric acid and some phosphates	Do.	*Ibid.*	1936, **3**, 25
32	Constitution of phosphorus acid and phosphites	R. Ananthakrishnan	*Nature*	1936, **138**, 803
33	A new technique of complementary filters for photographing Raman spectra of crystal powders	Do.	*Curr. Sci.*	1936, **5**, 131
34	Raman spectra of crystal powders. Part I. Halides and sulphates of ammonium	Do.	*Proc. Ind. Acad. Sci.*	1937, **5**, 76
35	Raman spectra of crystal powders. Part II. Chlorides and sulphates of hydroxylamine and hydrazine	Do.	*Ibid.*	1937, **5**, 87
36	Raman spectra of crystal powders. Part III. Exchange reactions of ammonium chloride and heavy water	Do.	*Ibid.*	1937, **5**, 175
37	Raman spectra of crystal powders. Part IV. Some organic and inorganic substances	Do.	*Ibid.*	1937, **5**, 200
38	Raman spectra of crystal powders. Part V. Inorganic nitrates and water of crystallisation	Do.	*Ibid.*	1937, **5**, 447
39	Note on the intensity of Raman lines in crystals	C. S. Venkateswaran	*Curr. Sci.*	1937, **6**, 92
40	Raman spectra of some inorganic compounds	Do.	*Proc. Ind. Acad. Sci.*	1938, **7**, 144
41	Scattering of light in sodium nitrate crystals	T. M. K. Nedungadi	*Ibid.*	1938, **8**, 397
42	A chart of Raman bands of water in crystals	P. G. N. Nayar	*Ibid.*	1938, **8**, 419
43	Low frequency Raman lines in organic crystals	C. S. Venkateswaran	*Ibid.*	1938, **8**, 448
44	The effect of crystal orientation on the Raman spectrum of sodium nitrate	T. M. K. Nedungadi	*Ibid.*	1939, **10**, 197

45	Effect of temperature on the Raman spectrum of quartz	Do.	*Ibid.*	1940, **11**, 86
46	Raman effect and crystal symmetry ..	B. D. Saxena	*Ibid.*	1940, **11**, 229
47	Raman effect in rochelle salt crystal ..	T. M. K. Nedungadi	*Ibid.*	1940, **11**, 413
48	Analysis of the Raman and infra-red spectrum of α-quartz	B. D. Saxena	*Ibid.*	1940, 12, 93
49	Raman spectrum of gypsum	Do.	*Ibid.*	1941, **13**, 25
50	Effect of crystal orientation on the Raman spectra of naphthalene and benzophenone	T. M. K. Nedungadi	*Ibid.*	1941, **13**, 161
51	Raman spectra of some crystalline nitrates and sulphates	B. Lakshmana Rao	*Ibid.*	1941, **14**, 48
52	Raman spectrum of potassium tartrate crystal	Do.	*Ibid.*	1941, **14**, 41
53	Studies in the Raman effect in single crystals of potassium nitrate	T. M. K. Nedungadi	*Ibid.*	1941, **14**, 242
54	The effect of crystal orientation on the Raman effect of barytes	T. A. S. Balakrishnan	*Ibid.*	1941, **14**, 257
55	Temperature variation of the Raman frequencies of diamond	P. G. N. Nayar	*Ibid.*	1941, 13, 284
56	Analysis of the Raman spectrum of single crystals of naphthalene	T. M. K. Nedungadi	*Ibid.*	1942, **15**, 376
57	Raman spectra of crystals excited by mercury resonance radiations	Roopkishore	*Ibid.*	1942, **16**, 36
58	Luminescence, absorption and scattering of light in diamond—Part IV	P. G. N. Nayar	*Ibid.*	1942, **15**, 310
59	Raman effect and change of state of naphthalene	R. Norris	*Ibid.*	1942, 16, 250
60	Raman spectrum of sulphur under high dispersion	Do.	*Ibid.*	1942, **16**, 287
61	Raman spectra of crystals and their interpretation	R. S. Krishnan	*Ibid.*	1943, **18**, 298
62	The Raman spectrum of diamond ..	Do.	*Ibid.*	1944, **19**, 216
63	Polarisation of Raman scattering and of fluorescence in diamond	A. Mani	*Ibid.*	1944, **20**, 117
64	Scattering of light in crystals	C. V. Raman	*Nature*	1945, **155**, 396
65	Raman spectrum of quartz	R. S. Krishnan	*Ibid.*	1945, **155**, 452

No.	Subject	Author	Journal	Year
66	Raman and infra-red absorption spectra of rock-salt	R. S. Krishnan	*Nature*	1945, **156**, 267
67	Raman spectra of the second order. Part I. Calcite	Do.	*Proc. Ind. Acad. Sci.*	1945, **22**, 182
68	Raman spectra of the second order. Part II. Gypsum	Do.	*Ibid.*	1945, **22**, 274
69	Raman spectra of the second order. Part III. Quartz	Do.	*Ibid.*	1945, **22**, 329
70	Raman spectra of the second order. Part IV. Barytes	Do.	*Ibid.*	1946, 23, 288
71	Raman effect in rock-salt	Do.	*Nature*	1946, **157**, 623
72	The Raman spectrum of rock-salt ..	Do.	*Proc. Roy. Soc. Lond.*	1946, **187**, 188
73	Second order Raman spectrum of diamond	Do.	*Proc. Ind. Acad. Sci.*	1946, **24**, 25
74	Temperature variation of the Raman frequencies of diamond	Do.	*Ibid.*	1946, **24**, 45
75	Raman spectrum of rock-salt under high resolution	Do.	*Nature*	1947, **159**, 266
76	Second order Raman spectra of crystals ..	Do.	*Ibid.*	1947, **160**, 230
77	Vibration spectra of alkali halides ..	Do.	*Ibid.*	1947, **160**, 711
78	The Raman spectrum of diamond under high resolution	Do.	*Ibid.*	1947, **159**, 60
79	Scattering of light in diamond and its Raman spectrum	Do.	*Proc. Ind. Acad. Sci.*	1947, **26**, 399
80	The Raman spectrum of rock-salt and its interpretation	Do.	*Ibid.*	1947, **26**, 419
81	The Raman spectrum of ammonium chloride and its variations with temperature	Do.	*Ibid.*	1947, **26**, 432
82	Influence of temperature on the Raman spectra of crystals. Part I. Calcite	P. K. Narayanaswamy	*Ibid.*	1947, **26**, 511
83	Influence of temperature on the Raman spectra of crystals. Part II. Quartz	Do.	*Ibid.*	1947, **26**, 521
84	Raman spectra of water, heavy water and ice	Do.	*Ibid.*	1948, **27**, 311
85	Raman spectrum of ammonium bromide and its variations with temperature	R. S. Krishnan	*Ibid.*	1948, **27**, 321

7. INFRA-RED SPECTRA

1	Infra-red spectrum of diamond ..	K. G. Ramanathan	*Nature*	1945, **156**, 23
2	The infra-red absorption spectrum of diamond	Do.	*Proc. Ind. Acad. Sci.*	1946, **24**, 150
3	Infra-red absorption spectrum of diamond	R. S. Krishnan and K. G. Ramanathan	*Nature*	1946, **157**, 45
4	Infra-red absorption spectrum of diamond	Do.	*Ibid.*	1946, **157**, 582
5	A home-made infra-red spectrometer ..	K. G. Ramanathan	*Curr. Sci.*	1946, **15**, 184
6	The infra-red spectrum	C. V. Raman	*Ibid.*	1947, **16**, 359
7	The infra-red absorption spectrum of diamond and its variations	K. G. Ramanathan	*Proc. Ind. Acad. Sci.*	1947, **26**, 469

8. LUMINESCENCE AND ABSORPTION

1	Cathode luminescence of diamond ..	M. V. John	*Ind. Jour. Phys.*	1931, **6**, 305
2	The fluorescence of ruby, saphire and emerald ..	C. S. Venkateswaran	*Proc. Ind. Acad. Sci.*	1935, **2**, 459
3	Luminescence, absorption and scattering of light in diamonds. Part I. Fluorescence	P. G. N. Nayar	*Ibid.*	1941, **13**, 483
4	Luminescence, absorption and scattering of light in diamonds. Part II. Phosphorescence	Do.	*Ibid.*	1941, **13**, 534
5	Luminescence, absorption and scattering of light in diamonds. Part III. Absorption	Do.	*Ibid.*	1941, **14**, 1
6	Fluorescence, absorption and scattering of light in ruby	A. Mani	*Ibid.*	1942, **15**, 52
7	Lattice and electronic spectrum of diamond	Do.	*Ibid.*	1942, **15**, 293
8	Spectroscopic investigation of the solid and liquid states	C. V. Raman	*Curr. Sci.*	1942, **11**, 225
9	Luminescence spectra and vibrations in crystal lattices	D. D. Pant	*Proc. Ind. Acad. Sci.*	1943, **18**, 309
10	Fluorescence spectrum of uranyl fluoride ..	D. D. Pant and N. D. Sakhwalkar	*Ibid.*	1944, **19**, 135
11	The fluorescence and absorption spectra of diamond in the visible region	A. Mani	*Ibid.*	1944, **19**, 231

No.	Subject	Author	Journal	Year
12	The ultraviolet absorption spectrum of diamond	K. Sunanda Bai	*Proc. Ind. Acad. Sci.*	1944, **19**, 253
13	Excitation curves of luminescence in diamond	A. Mani	*Ibid.*	1945, **21**, 280
14	Some studies in the spectra of single uranyl halides and other uranyl salts	D. D. Pant	*Ibid.*	1945, **22**, 95
15	Analysis of the fluorescence bands of the uranyl salts	Do.	*Ibid.*	1945, **22**, 110
16	The luminescence of diamond excited by X-radiation	G. N. Ramachandran	*Ibid.*	1946, **24**, 81
17	The absorption of ultra-violet radiation by diamond	K. G. Ramanathan	*Ibid.*	1946, **24**, 137
18	The absorption spectrum of diamond in the visible region	Do.	*Ibid.*	1946, **24**, 145
19	Luminescence as "Forbidden" electronic transition in diamond	G. N. Ramachandran and V. Chandrasekharan	*Ibid.*	1946, **24**, 176
20	The thermo-luminescence of diamond ..	V. Chandrasekharan	*Ibid.*	1946, **24**, 187
21	The phosphorescence of diamond ..	Do.	*Ibid.*	1946, **24**, 193
22	The emission and absorption spectra of luminescent diamonds	K. G. Ramanathan	*Ibid.*	1947, **26**, 479
23	The Raman spectrum of alumina and the luminescence and absorption spectra of ruby	R. S. Krishnan	*Nature*	1947, **160**, 26
24	Raman spectrum of alumina and the luminescence of ruby	Do.	*Proc. Ind. Acad. Sci.*	1947, **26**, 450
25	The Raman effect in topaz and its relation to the luminescence spectrum	Do.	*Ibid.*	1947, **26**, 460
26	Fluorescence and phosphorescence of diamond at different temperatures	V. Chandrasekharan	*Ibid.*	1948, **27**, 316

9. LATTICE DYNAMICS

1	The dynamical theory of the diamond lattice—Part I	N. S. Nagendra Nath	*Proc. Ind. Acad. Sci.*	1934, **1**, 333
2	The dynamical theory of the diamond lattice. Part II. The elastic constants of diamond	Do.	*Ibid.*	1934, **1**, 841
3	The dynamical theory of the diamond lattice. Part III. The diamond—graphite transformation	Do.	*Ibid.*	1935, **2**, 143
4	Lattice oscillations in crystals	C. V. Raman and T. M. K. Nedungadi	*Nature*	1939, **143**, 679
5	Vibration spectrum of a crystal lattice ..	C. V. Raman	*Proc. Ind. Acad. Sci.*	1943, **18**, 237
6	Normal vibrations of some typical cubic crystals	E. V. Chelam	*Ibid.*	1943, **18**, 257
7	Modes of atomic vibrations in fourteen Bravais lattices	G. N. Ramachandran	*Ibid.*	1943, **18**, 266
8	The normal vibrations of crystal lattices: Application of group theory	E. V. Chelam	*Ibid.*	1943, **18**, 283
9	Character tables for four cubic crystals ..	Do.	*Ibid.*	1943, **18**, 327
10	Vibrations of a close packed hexagonal lattice	G. N. Ramachandran	*Ibid.*	1943, **18**, 341
11	Fundamentals of crystal physics ..	C. V. Raman	*Curr. Sci.*	1943, **12**, 342
12	The vibration spectra of crystals. Part I. Basic theory	Do.	*Proc. Ind. Acad. Sci.*	1947, **26**, 339
13	The vibration spectra of crystals. Part II. The case of diamond	Do.	*Ibid.*	1947, **26**, 356
14	The vibration spectra of crystals. Part III. Rock-salt	Do.	*Ibid.*	1947, **26**, 370
15	The vibration spectra of crystals. Part IV. Magnesium oxide	Do.	*Ibid.*	1947, **26**, 383
16	The vibration spectra of crystals. Part V. Lithium and sodium fluorides	Do.	*Ibid.*	1947, **26**, 391
17	The vibration spectra of crystals. Part VI. Sylvine	Do.	*Ibid.*	1947, **26**, 396

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18	Dynamical theory of the vibration spectra of crystals. Part I. Diamond	K. G. Ramanathan	*Proc. Ind. Acad. Sci.*	1947, **26**, 481
19	Dynamical theory of the vibration spectra of crystals. Part II. Rock-salt structure	Do.	*Ibid.*	1947, **26**, 493
20	Dynamical theory of the vibration spectra of crystals. Part III. Cæsium chloride structure	Do.	*Ibid.*	1947, **26**, 500
21	Dynamical theory of the vibration spectra of crystals. Part IV. The metallic crystals	Do.	*Ibid.*	1947, **26**, 507
22	The eigenvibrations of crystal structures	C. V. Raman	*Curr. Sci.*	1948, **17**, 1

10. SPECIFIC HEAT AND THERMAL EXPANSION

1	Specific heat in relation to Raman effect data	S. Paramasivan	*Ind. Jour. Phys.*	1931, **6**, 413
2	The Raman spectrum and the specific heat of crystalline sulphur	R. Norris	*Proc. Ind. Acad. Sci.*	1941, **13**, 291
3	The thermal energy of crystalline solids: Basic theory	C. V. Raman	*Ibid.*	1941, **14**, 459
4	The thermal energy of crystalline solids: White phosphorus	R. Norris	*Ibid.*	1941, **14**, 468
5	The thermal energy of crystalline solids: Diamond	V. B. Anand	*Ibid.*	1941, **14**, 484
6	The thermal energy of crystalline solids: Lithium, tungsten, gold, silicon and grey tin	Bisheshwar Dayal	*Ibid.*	1941, **14**, 473
7	The thermal energy of crystalline solids: Magnesium, zinc and cadmium	Do.	*Ibid.*	1941, **14**, 492
8	The thermal energy of crystalline solids: Alkali halides	C. S. Venkateswaran	*Ibid.*	1941, **14**, 506
9	The thermal energy of crystalline solids: Quartz	R. Norris	*Ibid.*	1941, **14**, 499

10	The evaluation of the specific heat of rock-salt by the new crystal dynamics	Bisheshwar Dayal	*Ibid.*	1944, **19**, 182
11	Specific heat of metals crystallising in the cubic system	Do.	*Ibid.*	1944, **20**, 24
12	Specific heat of alkali halides	Do.	*Ibid.*	1944, **20**, 77
13	Specific heat of metallic silicon	Do.	*Ibid.*	1944, **20**, 87
14	Thermal expansion of diamond	B. D. Saxena	*Ibid.*	1944, **20**, 92
15	Lattice spectrum, specific heat and thermal expansion of lithium and sodium fluorides	Bisheshwar Dayal	*Ibid.*	1944, **20**, 138
16	A theory of the thermal expansion of alkali halides	Do.	*Ibid.*	1944, **20**, 145
17	The thermal expansion of diamond ..	Do.	*Ibid.*	1944, **20**, 187
18	The thermal expansion of metals at low temperatures	Do.	*Ibid.*	1944, **20**, 192
19	The lattice spectrum and specific heat of diamond	Do.	*Ibid.*	1944, **19**, 224
20	The thermal expansion of solids	C. V. Raman	*Curr. Sci.*	1944, **13**, 295
21	Thermal expansion of diamond ..	R. S. Krishnan	*Proc. Ind. Acad. Sci.*	1946, **24**, 33

11. DYNAMIC REFLECTION OF X-RAYS

1	A new X-ray effect	C. V. Raman and P. Nilakantan	*Curr. Sci.*	1940, **9**, 165
2	Specular reflection of X-rays by high frequency sound waves	Do.	*Nature*	1940, **145**, 667
3	Reflection of X-rays with change of frequency. Part I. Theoretical discussions	Do.	*Proc. Ind. Acad. Sci.*	1940, **11**, 379
4	Reflection of X-rays with change of frequency. Part II. The case of diamond	Do.	*Ibid.*	1940, **11**, 389
5	Reflection of X-rays with change of frequency. Part III. The case of sodium nitrate	Do.	*Ibid.*	1940, **11**, 398
6	The quantum theory of X-ray reflection and scattering. Part I. Geometric relations	C. V. Raman and N. S. Nagendra Nath	*Ibid.*	1940, **12**, 83

No.	Subject	Author	Journal	Year
7	Reflections of X-rays with change of frequency. Part IV. The case of rock-salt	C. V. Raman and P. Nilakantan	*Proc. Ind. Acad. Sci.*	1940, **12**, 141
8	The two types of X-ray reflections in crystals	C. V. Raman and N. S. Nagendra Nath	*Ibid.*	1940, **12**, 427
9	Modified reflection of X-rays	C. V. Raman and P. Nilakantan	*Nature*	1940, **146**, 523
10	Classical and quantum reflection of X-rays in crystals	Do.	*Ibid.*	1940, **146**, 686
11	Quantum theory of X-ray reflection: Basic ideas	C. V. Raman	*Proc. Ind. Acad. Sci.*	1941, **14**, 317
12	Quantum theory of X-ray reflection: Mathematical formulation	Do.	*Ibid.*	1941, **14**, 332
13	Quantum theory of X-ray reflection: Experimental confirmation	C. V. Raman and P. Nilakantan	*Ibid.*	1941, **14**, 356
14	A quantum theoretical explanation of the appearance of forbidden X-ray reflections in diamond	P. Rama Pisharoti	*Ibid.*	1941, **14**, 377
15	Low temperature studies of the Raman X-ray reflections in crystals	C. S. Venkateswaran	*Ibid.*	1941, **14**, 387
16	The quantum reflections and the quantum scattering of X-rays by rock-salt	Do.	*Ibid.*	1941, **14**, 395
17	The Raman X-ray reflection in organic crystals: I. Naphthalene	Do.	*Ibid.*	1941, **14**, 402
18	The Raman X-ray reflection in organic crystals: II. Benzophenone	Do.	*Ibid.*	1941, **14**, 409
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1	Crystal structure of para-nitro-toluene	B. N. Sreenivasiah	*Ind. Jour. Phys.*	1928, **2**, 151
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4	Structure of some organic crystals	S. Bhagavantam	*Proc. Inst. Chem.*	1929, **2**, 15
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9	X-ray analysis of the structure of diphenyl	J. Dhar	*Ibid.*	1932, **7**, 43
10	X-ray analysis of the structure of iridescent shells—Part I	S. Rama Swamy	*Proc. Ind. Acad. Sci.*	1935, **1**, 871
11	X-ray analysis of the structure of iridescent shells—Part II	Do.	*Ibid.*	1935, **2**, 345

No.	Subject	Author	Journal	Year
12	The structure of thin metallic films ..	S. Rama Swamy	*Proc. Ind. Acad. Sci.*	1936, **4**, 656
13	X-ray studies of wood lignin and wood cellulose	P. Nilakantan	*Ibid.*	1937, **5**, 166
14	X-ray analysis of the structure of a fibrous modification of tourmaline	S. Rama Swamy and K. Y. S. Iyengar	*Ibid.*	1937, 5, 419
15	New concepts of crystal structure ..	C. V. Raman	*Curr. Sci.*	1946, **15**, 329

13. STRUCTURE AND PROPERTIES OF DIAMOND

No.	Subject	Author	Journal	Year
1	Physics of the diamond	C. V. Raman	*Curr. Sci.*	1942, **11**, 261
2	The structure and properties of diamond ..	Do.	*Ibid.*	1943, **12**, 33
3	The four forms of diamond	Do.	*Ibid.*	1944, **13**, 145
4	The crystal symmetry and structure of diamond	Do.	*Proc. Ind. Acad. Sci.*	1944, **19**, 189
5	The nature and origin of the luminescence of diamond	Do.	*Ibid.*	1944, **19**, 199
6	Intensity of X-ray reflection by diamond ..	P. S. Hariharan	*Ibid.*	1944, **19**, 261
7	Birefringence patterns in diamond ..	C. V. Raman and G. R. Rendall	*Ibid.*	1944, **19**, 265
8	Luminescence patterns in diamond ..	K. Sunanda Bai	*Ibid.*	1944, **19**, 274
9	X-ray topographs of diamond	G. N. Ramachandran	*Ibid.*	1944, **19**, 280
10	Ultra-violet transparency patterns in diamond	G. R. Rendall	*Ibid.*	1944, **19**, 293
11	Experimental evidence for the four possible structures of diamond	R. S. Krishnan	*Ibid.*	1944, **19**, 298
12	X-ray reflection and the structure of diamond	G. N. Ramachandran	*Ibid.*	1944, 19, 304
13	The crystal forms of the Panna diamonds ..	S. Ramaseshan	*Ibid.*	1944, **19**, 334
14	Spectroscopic study of luminescence patterns in diamond	A. Mani	*Ibid.*	1944, **20**, 155
15	Fluorescence and absorption patterns in diamond at low temperature	Do.	*Ibid.*	1944, **20**, 323
16	X-ray topographs of diamond	G. N. Ramachandran	*Curr. Sci.*	1944, **13**, 156

17	The angular divergence of the X-ray reflections by diamond	Do.	*Proc. Ind. Acad. Sci.*	1944, **20**, 245
18	The crystal forms of diamond and their significance	C. V. Raman and S. Ramaseshan	*Ibid.*	1946, **24**, 1
19	On the crystal symmetry of diamond and its X-ray reflections	G. N. Ramachandran	*Ibid.*	1946, **24**, 58
20	On the nature and origin of the laminations observed in diamond	Do.	*Ibid.*	1946, **24**, 65
21	X-ray topographs of diamond	Do.	*Ibid.*	1946, **24**, 95
22	The cleavage properties of diamond ..	S. Ramaseshan	*Ibid.*	1946, **24**, 114
23	A theory of the crystal forms of diamond ..	Do.	*Ibid.*	1946, **24**, 122
24	Variation in the absorption of infra-red radiations by diamond	K. G. Ramanathan	*Ibid.*	1946, **24**, 130
25	Local variations in the photo-conductivity of diamond	K. Achyuthan	*Ibid.*	1946, **24**, 162
26	Geometric patterns of fluorescence in diamond	G. R. Rendall	*Ibid.*	1946, **24**, 168
27	Phosphorescence patterns in diamond ..	V. Chandrasekharan	*Ibid.*	1946, **24**, 182
28	Allotropic modifications of diamond ..	C. V. Raman	*Nature*	1945, **156**, 22
29	Crystal structure of diamond	G. N. Ramachandran	*Ibid.*	1945, **156**, 83
30	The diamond and its teachings	C. V. Raman	*Curr. Sci.*	1946, **15**, 205
31	Directional variations in the photoconductivity of diamond	K. Achyuthan	*Proc. Ind. Acad. Sci.*	1948, **27**, 171

14. MISCELLANEOUS

1	The elastic properties of mother of pearl ..	P. S. Srinivasan	*Proc. Ind. Acad. Sci.*	1937, **5**, 463
2	Young's modulus of diamond	P. R. Pisharoti	*Ibid.*	1940, **12**, 208
3	α-β transformation of quartz	C. V Raman and T. M. K. Nedungadi	*Nature*	1940, **145**, 147
4	Crystals and photons	C. V. Raman	*Proc. Ind. Acad. Sci.*	1941, **13**, 1
5	New concepts of the solid state	Do.	*Curr. Sci.*	1942, **11**, 85
6	X-rays, crystals and the infra-red spectrum	Do.	*Ibid.*	1941, **10**, 473
7	The photo-conductivity of diamond—Part I	D. D. Pant	*Proc. Ind. Acad. Sci.*	1944, **19**, 315
8	The photo-conductivity of diamond—Part II	Do.	*Ibid.*	1944, **19**, 325

PREFATORY NOTE TO THE SYMPOSIUM

THE present Symposium published in commemoration of the Sixtieth Birthday of Sir C. V. Raman consists of twenty-nine papers dealing with various aspects of the subject of Crystal Physics. Shortness of time stood in the way of its being made more fully representative and the range of topics dealt with in it more comprehensive. That it has been possible to include a few contributions by distinguished investigators in other countries is due to the great kindness of these authors in responding to the invitation of the Council in spite of the extremely short notice given to them. Professors Forrest F. Cleveland, R. Bowling Barnes, N. F. Mott, Linus Pauling, C. Manneback, Robert Hoftstadter, R. W. G. Wycoff and Geo. Glockler, who were invited to contribute but were unable to send papers, have sent very kind messages conveying their good wishes and felicitations. To them and to all those who have contributed to the Symposium, the Council wish to express their grateful thanks.

THE VIBRATIONS OF AN INFINITE LINEAR LATTICE CONSISTING OF TWO TYPES OF PARTICLES

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THE vibrations of a finite linear lattice of equal masses were first investigated by Lagrange,[1] assuming the end particles to be at rest and those of an infinite linear lattice by Hamilton.[2] The former work is well quoted in connection with the vibrations of strings and Fourier series, while Hamilton's work has not been properly appreciated.[3]

In this paper the vibrations of an infinite linear lattice consisting of two types of particles have been investigated. We consider a lattice consisting of two types of particles of masses m_1 and m_2 alternating one another at equal distances and in stable equilibrium. At time $t = 0$, one of the particles is given an arbitrary but small displacement a along the lattice and all the others are at rest in their equilibrium configurations. We assume that the forces acting on a particle arise due to changes in the positions of all the particles and are proportional to them. Later in the paper, we shall make certain simplifying assumptions in order to find out the asymptotic nature of the vibrations. We denote the displacements of the particles at the instant of time t by $x_m(t)$ where m is any integer ranging from $-\infty$ to $+\infty$. The initial conditions are given by $x_m(0) = 0$ for all m except $m = 0$, $x_0(0) = a$ and $\dot{x}_m(0) = 0$ for all m.

The equations of motion of the $2r$th and $(2r+1)$th particles are

$$\begin{aligned} -m_1\ddot{x}_{2r} &= B_0 x_{2r} + \sum_{s=1}^{\infty} B_{2s}\,(x_{2r+2s} + x_{2r-2s}) \\ &\quad + \sum_{s=0}^{\infty} B_{2s+1}\,(x_{2r+2s+1} + x_{2r-2s-1}), \\ -m_2\ddot{x}_{2r+1} &= C_0 x_{2r+1} + \sum_{s=1}^{\infty} C_{2s}\,(x_{2r+2s+1} + x_{2r-2s+1}) \\ &\quad + \sum_{s=0}^{\infty} B_{2s+1}\,(x_{2r+2s+2} + x_{2r-2s}). \end{aligned} \tag{1}$$

We seek solutions of the type

$$x_{2r} = f(\phi)\, e^{i(\omega t - r\phi)}, \quad x_{2r+1} = g(\phi)\, e^{i(\omega t - r\phi)} \tag{2}$$

where ω, f and g are functions of the real parameter ϕ.

Substituting (2) in the equations of motion (1) and removing common factors, we get

$$\left[B_0 + 2\sum_1^{\infty} B_{2s}\cos s\phi - \omega^2 m_1\right] f(\phi) + 2\left[\sum_0^{\infty} B_{2s+1}\, e^{\frac{i\phi}{2}} \cos\left(s+\tfrac{1}{2}\right)\phi\right] g(\phi) = 0,$$

$$2\left[\sum_0^{\infty} B_{2s+1}\, e^{-\frac{i\phi}{2}} \cos\left(s+\tfrac{1}{2}\right)\phi\right] f(\phi) + \left[C_0 + 2\sum_1^{\infty} C_{2s}\cos s\phi - \omega^2 m_2\right] g(\phi) = 0.$$

Eliminating $f(\phi)$ and $g(\phi)$ in (3), we find that ω satisfies the equation

$$\begin{aligned} m_1 m_2 \omega^4 - \omega^2 &\left[m_1 C_0 + m_2 B_0 + 2\sum_1^{\infty}(m_1 C_{2s} + m_2 B_{2s})\cos s\phi\right] \\ &+ \left[C_0 + 2\sum_1^{\infty} C_{2s}\cos s\phi\right]\left[B_0 + 2\sum_1^{\infty} B_{2s}\cos s\phi\right] \\ &\qquad - 4\left[\sum_0^{\infty} B_{2s+1}\cos\left(s+\tfrac{1}{2}\right)\phi\right]^2 = 0. \qquad (4) \end{aligned}$$

The equation gives four values of ω for each ϕ, which we shall denote by ω_1, ω_2, $-\omega_1$, $-\omega_2$ and the corresponding values of $f(\phi)$ and $g(\phi)$ will be denoted by f_1, f_2, f_3, f_4 and g_1, g_2, g_3, g_4. The general solutions can be built up by the superposition of the solutions of the type (2) within the range of ϕ between 0 and 2π. Since the period of ω is 2π, there is no use in repeating the values of ω over and over again by assigning to ϕ, values outside the range. The general solutions of (1) can now be written as

$$x_{2r} = \frac{1}{4\pi}\int_0^{2\pi} \left\{f_1(\phi)\, e^{i\omega_1 t} + f_2(\phi)\, e^{i\omega_2 t} + f_3(\phi)\, e^{-i\omega_1 t} + f_4(\phi)\, e^{-i\omega_2 t}\right\} e^{-ir\phi}\, d\phi,$$

$$x_{2r+1} = \frac{1}{4\pi}\int_0^{2\pi} \left\{g_1(\phi)\, e^{i\omega_1 t} + g_2(\phi)\, e^{i\omega_2 t} + g_3(\phi)\, e^{-i\omega_1 t} + g_4(\phi)\, e^{-i\omega_2 t}\right\} e^{-ir\phi}\, d\phi. \qquad (5)$$

From equations (3), we get

$$f_1(\phi) = \lambda(\phi)\, g_1(\phi),\ f_2(\phi) = \mu(\phi)\, g_2(\phi),\ f_3(\phi) = \lambda(\phi)\, g_3(\phi),\ f_4(\phi) = \mu(\phi)\, g_4(\phi) \qquad (6)$$

where $$\lambda(\phi) = \frac{m_2\omega_1^2 - \left[C_0 + 2\sum_1^{\infty} C_{2s}\cos s\phi\right]}{2\sum_0^{\infty} B_{2s+1}\, e^{-\frac{i\phi}{2}}\cos\left(s+\tfrac{1}{2}\right)\phi}$$ and

$$\mu(\phi) = \frac{m_2\omega_2^2 - \left[C_0 + 2\sum_1^{\infty} C_{2s}\cos s\phi\right]}{2\sum_0^{\infty} B_{2s+1}\, e^{-\frac{i\phi}{2}}\cos\left(s+\tfrac{1}{2}\right)\phi}.$$

The second equation in (5) can now be written as

$$x_{2r+1}=\frac{1}{4\pi}\int_0^{2\pi}\left\{\frac{f_1(\phi)\,e^{i\omega_1 t}+f_3(\phi)\,e^{-i\omega_1 t}}{\lambda(\phi)}+\frac{f_2(\phi)\,e^{i\omega_2 t}+f_4(\phi)\,e^{-i\omega_2 t}}{\mu(\phi)}\right\}e^{-ir\phi}\,d\phi. \tag{7}$$

The boundary conditions are given by $x_0(0)=a$, $x_m(0)=0$ for all m except $m=0$ and $\dot{x}_m(0)=0$ for all m. Hence from the expressions for x_{2r} and x_{2r+1}, we get

$$\begin{aligned}
&\int_0^{2\pi}(f_1+f_2+f_3+f_4)\,d\phi=4\pi a,\\
&\int_0^{2\pi}(f_1+f_2+f_3+f_4)\,e^{-ir\phi}\,d\phi=0,\ \text{ for all } r \text{ except } r=0,\\
&\int_0^{2\pi}\left(\frac{f_1+f_3}{\lambda}+\frac{f_2+f_4}{\mu}\right)e^{-ir\phi}\,d\phi=0,\\
&\int_0^{2\pi}\omega_1(f_1-f_3)+\omega_2(f_2-f_4)\,e^{-ir\phi}\,d\phi=0,\\
&\int_0^{2\pi}\left\{\frac{\omega_1}{\lambda}(f_1-f_3)+\frac{\omega_2}{\mu}(f_2-f_4)\right\}e^{-ir\phi}\,d\phi=0,
\end{aligned} \tag{8}$$

the last three equations being true for all integral values of r.

Thus,

$$\begin{aligned}
&f_1+f_2+f_3+f_4=2a,\\
&\mu(f_1+f_3)+\lambda(f_2+f_4)=0,\\
&\omega_1(f_1-f_3)+\omega_2(f_2-f_4)=0,\\
&\omega_1\mu(f_1-f_3)+\omega_2\lambda(f_2-f_4)=0.
\end{aligned} \tag{9}$$

From these equations it follows that

$$f_1=\frac{a\lambda}{\lambda-\mu},\ f_2=\frac{a\mu}{\mu-\lambda},\ f_3=f_1,\ f_4=f_2. \tag{10}$$

The solutions under the specified boundary conditions, can now be written as

$$\begin{aligned}
x_{2r}=&\frac{a}{2\pi}\int_0^{2\pi}\frac{m_2\omega_1^2-\left[C_0+2\sum_1^{\infty}C_{2s}\cos s\phi\right]}{m_2(\omega_1^2-\omega_2^2)}\,e^{-ir\phi}\cos\omega_1 t\,d\phi\\
&+\frac{a}{2\pi}\int_0^{2\pi}\frac{m_2\omega_2^2-\left[C_0+2\sum_1^{\infty}C_{2s}\cos s\phi\right]}{m_2(\omega_2^2-\omega_1^2)}\,e^{-ir\phi}\cos\omega_2 t\,d\phi,
\end{aligned}$$

and

$$x_{2r+1} = \frac{a}{\pi}\int_0^{2\pi} \frac{\sum_0^{\infty} B_{2s+1} e^{-\frac{i\phi}{2}} \cos (s+\frac{1}{2})\phi}{m_2(\omega_1^2-\omega_2^2)} (\cos \omega_1 t - \cos \omega_2 t)\, e^{-ir\phi}\, d\phi. \tag{11}$$

We now make the simplifying assumption that the forces acting on a particle arise only due to changes in the neighbouring distances. This case is obtained by putting $B_{2s} = C_{2s} = 0$ for all s, except B_0 and C_0 and all $B_{2s+1} = 0$ except B_1. We shall put $2a = \frac{B_0}{m_1}$, $2b = \frac{C_0}{m_2}$, $am_1 = bm_2 = -B_1$ and $z = e^{i\phi}$, so that ω_1, ω_2, $-\omega_1$ and $-\omega_2$ are now the roots of

$$z\omega^4 - 2z\omega^2(a+b) - ab(z-1)^2 = 0, \tag{12}$$

and the solutions are given by

$$x_{2r} = \frac{a}{2\pi i}\int_C \frac{(\omega_1^2 - 2b)\cos \omega_1 t}{(\omega_1^2 - \omega_2^2)\, z^{r+1}}\, dz + \frac{a}{2\pi i}\int_C \frac{(\omega_2^2 - 2b)\cos \omega_2 t}{(\omega_2^2 - \omega_1^2)\, z^{r+1}}\, dz,$$

and

$$x_{2r+1} = \frac{a}{2\pi i}\int_C \frac{b(1+z)(\cos \omega_2 t - \cos \omega_1 t)}{(\omega_1^2 - \omega_2^2)\, z^{r+2}}\, dz, \tag{13}$$

which can be expressed in the form

$$x_{2r} = \frac{1}{4\pi i}\oint \frac{f(z)\, e^{i\omega t}}{z^{r+1}}\, dz, \quad x_{2r+1} = \frac{1}{4\pi i}\oint \frac{g(z)\, e^{i\omega t}}{z^{r+1}}\, dz, \tag{14}$$

where ω is a four-valued function given by the equation (12) and *the path of the integral is a closed curve on the four-sheeted Riemann surface for* $\omega(z)$.

The Riemann surface for $\omega(z)$ is given by

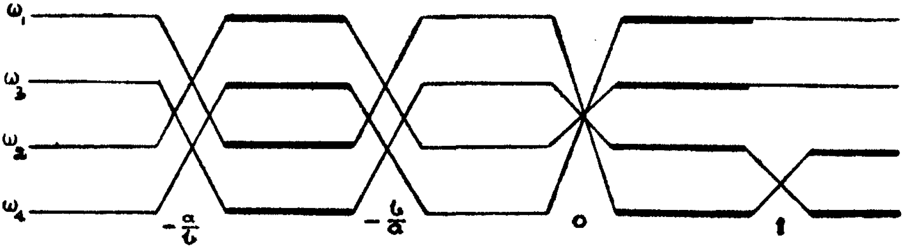

FIG. 1

The thick lines are cuts along which the surfaces are connected for the passage from one plane to the other. $\omega(z)$ is a holomorphic function of z on this four-sheeted surface.

We shall find the asymptotic nature of the solutions by the method of steepest descents. We select the contour of integration in (13) in such a way that it coincides with the paths of the steepest descents.

The equations (13) can be written in the form

$$x_{2r} = \frac{a}{8\pi i} \oint \frac{e^{i\omega_1 t} + e^{-i\omega_1 t} + e^{i\omega_2 t} + e^{-i\omega_2 t}}{z^{r+1}}\, dz$$

$$+ \frac{a(a-b)}{8\pi i} \oint \frac{e^{i\omega_1 t} + e^{-i\omega_1 t} - e^{i\omega_2 t} - e^{-i\omega_2 t}}{z^{r+1}\sigma}\, dz,$$

and

$$x_{2r+1} = \frac{a}{8\pi i} \oint \frac{b(1+z)(e^{i\omega_2 t} + e^{-i\omega_2 t} - e^{i\omega_1 t} - e^{-i\omega_1 t})}{z^{r+2}\sigma}\, dz, \tag{15}$$

where $2\sigma = \omega_1^2 - \omega_2^2$ and $\omega_1^2 = a + b + \sigma$, $\omega_2^2 = a + b - \sigma$.

The above expressions are the sum of terms of the form

$$\mathrm{P} = \oint \mathrm{R}(z)\, e^{\omega(z)t}\, dz. \tag{16}$$

The saddle points are given by $\frac{d\omega}{dz} = 0$. If z_0 be a saddle point then the asymptotic value of P is given by[4]

$$\frac{\mathrm{R}(z_0)\, e^{\omega(z_0)t} \sqrt{2\pi}\, e^{i\theta}}{|\, t\omega''(z_0)\,|^{\frac{1}{2}}} \tag{17}$$

where θ denotes the angle that the path of the steepest descents makes with the real axis and its value is to be found in each case by the usual method.

We shall first assume that $a > b$. The saddle points are given by $\omega_1' = 0$, $\omega_2' = 0$, that is by $z = \pm 1$. At the point $z = 1$, $\omega_1(z)$ has a development in powers of $(z-1) = z'$ of the type $\mathrm{A} + \mathrm{B}z'^2 + \ldots$ where z' is small and $\mathrm{B} > 0$; therefore, the behaviour of $i\omega_1$ at $z = 1$ is like that of iz'^2. Putting $z' = \xi + i\eta$, we have $i\omega_1(z) = \phi + i\psi = i(\xi^2 - \eta^2) - 2\xi\eta$. Now $\psi = 0$ gives the lines of steepest descents and they are therefore given by $\xi = \pm\eta$, (ξ, η) being the set of rectangular axes at $z = 1$ as origin, the ξ-axis coinciding with the real axis. Also $\phi = -2\xi\eta$ and ϕ has to decrease as we proceed along the lines of steepest descents. ϕ will decrease if both ξ and η be positive or if both of them be negative. Taking the counter-clockwise direction as the path of integration we get $\theta = \frac{1}{4}\pi$. Similarly at $z = -1$ we get $\theta = \frac{3}{4}\pi$. For $i\omega_2(z)$ we get at $z = 1$, $\theta = \frac{3}{4}\pi$ and at $z = -1$, $\theta = \frac{5}{4}\pi$.

After substituting in (17) the values of θ, $\mathbf{R}(z_0)$, etc., we get after some reduction,

$$x_{2r} = a\left(\frac{a}{b}\right)^{\frac14}\left(\frac{2}{\pi\vartheta_1 t}\right)^{\frac12}\cos\left(\vartheta_1 t - \frac{\pi}{4}\right)$$
$$+ (-1)^r a\left\{\frac{|a-b|}{b}\right\}^{\frac14}\left(\frac{2}{\pi\vartheta_2 t}\right)^{\frac12}\cos\left(\vartheta_2 t + \frac{\pi}{4}\right) \qquad (18)$$

where $\vartheta_1 = \sqrt{2a+2b}$, $\vartheta_2 = \sqrt{2a}$.

Similarly the asymptotic value of x_{2r+1} is given by

$$x_{2r+1} = -a\left(\frac{b}{a}\right)^{\frac14}\left(\frac{2}{\pi\vartheta_1 t}\right)^{\frac12}\cos\left(\vartheta_1 t - \frac{\pi}{4}\right) \qquad (19)$$

In case $b > a$, the phase $\frac{\pi}{4}$ in the second term of (18) will be changed to $-\frac{\pi}{4}$.

The normal vibrations of the lattice according to Raman are given below:—

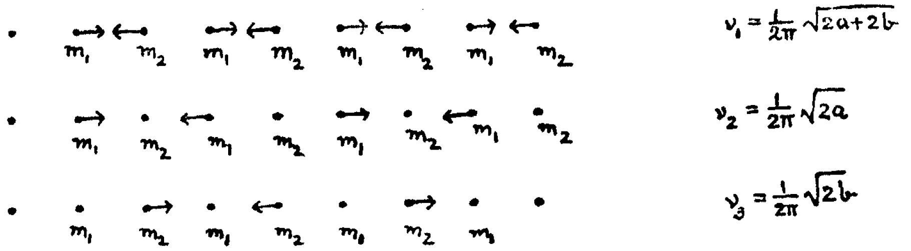
m_1
m_2
$\nu_1 = \frac{1}{2\pi}\sqrt{2a+2b}$
$\nu_2 = \frac{1}{2\pi}\sqrt{2a}$
$\nu_3 = \frac{1}{2\pi}\sqrt{2b}$

FIG. 2

If the lattice at the time $t = 0$ is disturbed as follows

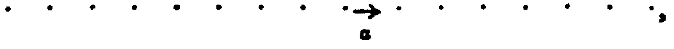

FIG. 3

the amplitudes of the particles for sufficiently large t are asymptotically given by (18) and (19) which show that the solutions tend to a time dependent superposition of normal solutions with frequencies ν_1 and ν_2. If however a particle with mass m_2 had been displaced, the asymptotic nature would have been a time dependent superposition of vibrations with frequencies ν_1 and ν_3. If either both m_1 and m_2 or an arbitrary finite set of particles of the lattice had been disturbed, we can say by the principle of superposition, *that the asymptotic nature of the vibration would tend to a time dependent superposition of the normal vibrations according to Raman.*

If $a = b$, the vibrations with frequencies ν_2 and ν_3 cease to be normal vibrations according to Raman. There is no discontinuity in the result of the above paragraph as $a \rightarrow b$ from that when $a = b$, for the controlling factors in the contributions of oscillations with frequencies ν_2 and ν_3 depend on $| a - b |$. *It may also be noted that when $a = b$, the oscillations ν_2 and ν_3 cease to be saddle point oscillations.* In this case x_{2r} and x_{2r+1} take the form[5] $J_{4r}(\sqrt{2a}t)$ and $J_{4r+2}(\sqrt{2a}t)$ corresponding to Hamilton's solutions.

SUMMARY

The solutions for the displacements of an infinite linear lattice consisting of two types of particles under some initial disturbance have been obtained and their asymptotic nature has been investigated by the method of "steepest descents" which shows that the displacements are asymptotically time dependent superposition of the normal vibrations according to Raman.

. . . .

I take this opportunity of recording here my indebtedness and gratitude to my Professor, Sir C. V. Raman, on the occasion of his sixtieth birthday.

N. S. NAGENDRA NATH.

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THE VIBRATION SPECTRA OF THE ALKALI HALIDES

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1. Introduction

The scattering of light in crystals comprises two different phenomena, the thermal scattering and the Raman effect. The former is due to the optical stratifications in the crystal associated with thermally excited stationary vibrations of the elastic type. The latter arises from the excitation of the vibrations of the atoms in a crystal by the radiations traversing it and is closely linked up with its vibration spectrum. Theoretical considerations and facts of observation alike indicate that we are here concerned, not with a coherent reflection as in the case of the thermal scattering, but with an incoherent scattering in which the process involved is the transfer of energy in discrete quanta between the radiation field and the individual volume elements of molecular dimensions in the crystal. This view of the phenomenon is indicated in the first place by the obvious points of similarity between the effects exhibited by crystals and those observed in the Raman scattering by gases and liquids. In the case of ionic or molecular crystals, vibrational frequency shifts appear as sharp lines and have nearly the same values as those observed with the same substance in the fluid state. In fact, the lines are generally sharper in the case of the crystal than in the liquid because of the more precise character of the force-fields in the crystalline medium. Overtones and summations of the fundamental frequencies are also recorded as sharp lines with observable intensities in the well-exposed spectrograms of numerous crystals like calcite, quartz, gypsum, barite, etc. (Krishnan, 1945 *a*, 1946 *a*). This is an indication that the amplitudes of the excited vibrations are not negligibly small in comparison with inter-atomic distances and that in consequence, the optical anharmonicity or lack of proportionality between the atomic displacements and the resulting variations of optical polarisabilities becomes operative. For this to be possible with an oscillator of which the energy is quantised and hence determinate, its dimensions should be of molecular order of magnitude.

In view of the situation stated above, it becomes evident that we are concerned with the evaluation of the normal modes of vibration of the structural units of which the crystal is composed. This is the problem which has been considered and solved by Sir C. V. Raman (1943, 1947) in two theoretical papers in these *Proceedings*. If there are p atoms in the unit cell of the crystal structure, one might think that there would be only $3p$ normal modes characteristic of the individual unit cells. But this is not actually the case because the influence of the neighbouring units on the oscillation of any particular unit cell has to be taken into consideration. Since the crystal consists of sets of equivalent atoms ordered in such a manner that each atom in a set is geometrically and physically related to its environment in exactly the same way as every other atom of the same set, the oscillations of the atoms in adjacent cells of the structure have to be alike in every respect except that the phases may be either the same or opposite along each axis of the lattice. Combining the three pairs of these alternative possibilities gives eight possibilities and therefore, eight times $3p$ or $24p$ modes of vibration as has been shown by Sir C. V. Raman. In $(3p-3)$ of these modes, equivalent atoms in adjacent cells have the same amplitudes and the same phase of vibration, while in the remaining $21p$ modes, they have the same amplitude but alternately opposite phases in successive cells along one, two, or all three axes of the space lattice. In relation to the entire crystal, the $(24p-3)$ oscillation frequencies are highly degenerate, being the characteristic frequencies of the group of $8p$ atoms in a volume element having twice the linear dimensions and eight times the volume of the lattice cells. The three excluded modes are the simple translations of such a volume element. Thus, if we approach the problem from the atomistic standpoint, the $(24p-3)$ modes are the only ones possible and they describe the vibration spectrum of the structure completely. In any actual case, the number of distinct frequencies would necessarily be less than $(24p-3)$ if the crystal possesses additional elements of symmetry. In the first order Raman effect, only the fundamentals of not more than $(3p-3)$ of these modes are active, while all the $(24p-3)$ modes can appear as overtones and summations in the second order Raman effect, thus yielding highly complex spectra which are necessarily of low intensity.*

A verification of the foregoing ideas is already forthcoming in the case of diamond from the results of a variety of studies on different aspects, namely, light-scattering, infra-red absorption, luminescence, ultra-violet absorption, etc. The considerations mentioned in the last paragraph are perfectly general and should be applicable to all crystals alike in such simple cases as the alkali halides and to complex ones such as quartz, topaz, organic crystals, etc. Detailed investigations on the Raman spectra of rock-salt, ammonium chloride and ammonium bromide carried out by one of us (R. S. Krishnan, 1945 *b*, 1946 *b*, 1947 *a*, 1948) have clearly established the discrete character of their vibration spectra, thus confirming the correctness of the theoretical ideas presented earlier in this section. The Raman spectrum of potassium bromide has now been studied by us and the results are presented in this paper.

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* The basic principles of lattice dynamics have been critically examined by Bhagavantam and Venkatarayudu in their book on *Group Theory and Its Application to Physical Problems*, Bangalore Press, 1948, Chapters X and XI, to which the reader may be referred.

2. EXPERIMENTAL DETAILS

Because of the ionic nature of the binding forces, and the heavy atomic weights of the ions in alkali halides, their vibration spectra are spread over a narrow range and the actual frequencies have low values. The large number of frequency shifts belonging to the second order Raman spectrum therefore appear crowded together. The spectrum exhibiting these frequency shifts is weak and is recorded near the exciting radiation which, unless it is completely eliminated, results with prolonged exposures in recording various spurious effects in its vicinity even with the best of instruments. Further, the fact that the vibration frequencies are low has the consequence that the vibrations will be thermally excited to an appreciable extent, giving rise to a broadening of the lines. If all these factors are taken into consideration, the resulting spectrum could easily be mistaken for a continuous one. In order to find the real nature of the spectrum, it may be necessary to use the highest possible dispersive and resolving powers. In spite of these difficulties, the very first photograph of the Raman spectrum of rock-salt taken by Rasetti with a medium quartz spectrograph showed the presence of a line at 235 cm.$^{-1}$ to the sharpness of which Rasetti drew special attention. Since then, detailed studies of the Raman spectrum of rock-salt under more favourable conditions of dispersion and resolution have not only confirmed Rasetti's observation but also shown the discrete character of the rock-salt spectrum unambiguously.

Potassium bromide has a crystal structure similar to that of rock-salt, but as the ions in the former are heavier, the Raman frequency shifts are smaller and hence less easy to record in a satisfactory manner. Menzies and Skinner (1948 *a, b*) who first photographed the spectrum of potassium bromide observed some details in the spectrum. In the present investigation, the authors have made considerable improvements in the experimental technique. By effecting a very perfect elimination of the diffuse continuum of instrumental origin and by using a large quartz spectrograph, the details of the KBr spectrum have been clearly brought out in the photograph.

Three specimens of synthetic potassium bromide were made available to us for the present study by the kindness of Dr. A. C. Menzies to whom the authors' thanks are due. One of them which had a slight yellowish tinge was found to be only partially transparent to the λ 2537 radiation and as such it had to be rejected. The second one was extremely clear and free from any colour. This had the following dimensions (2″ × 1½″ × 1″). Using this specimen and a medium quartz spectrograph with a fine slit (0·025 mm.) an exposure of about 4 hours was sufficient to record all the features of the spectrum. However, longer exposures of the order of 24 hours were given to get intense photographs. The experiment was repeated with a Hilger large quartz spectrograph. Due to prolonged exposure to the rays from the mercury arc, this crystal acquired a distinct colouration and a diminished transparency and the spectrum was, therefore, not recorded with the full intensity hoped for even after an exposure of 15 days. The third specimen (4″ × 2″ × 1½″) which was not as clear as the second one was also found to be partially opaque in thick layers to the λ 2537 radiations. Using this, moderately intense spectrograms were taken with the large quartz spectrograph with a moderate slit width and an exposure of ten days. The negatives were measured with the aid of a Hilger cross slide micrometer.

3. RESULTS

The spectrogram taken with the medium quartz spectrograph having a slit width of 0·025 mm. and an exposure of 24 hours is reproduced together with the microphotometer record of a lighter negative as Figs. 1 (*a*) and (*b*) respectively in the Plate. As is evident from the reproduced photograph, the spectrum of potassium bromide is confined to a region of frequency shifts from 46 cm.$^{-1}$ to about 290 cm.$^{-1}$ It consists of a series of distinct Raman lines with frequency shifts 46 (5), 84 (6), 126 (10), 146 (9), 170 (5), 186 (3), 216 (5), 228 (2), 232 (2), 242 (2) and 287 (1) cm.$^{-1}$ They can be easily distinguished in the photograph. Their positions have been marked in the microphotometer record. The figures given in brackets represent visual estimates of the relative intensities of the lines. Menzies and Skinner (1948 *b*) were able to identify only seven frequency shifts in the spectrogram taken by them. The values agree reasonably well with those reported by them. Our photographs show greater detail than the ones taken by Menzies and Skinner* evidently due to better technique of experimentation and more efficient filtering of the exciting radiation.

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* Dr. Menzies informs us that they have recently succeeded in getting good photographs showing as many details as those taken by us.

The most conspicuous feature in the spectrum of potassium bromide is the extreme sharpness of the lines 84, 126, 146, 170 and 216 cm.$^{-1}$ The corresponding anti-Stokes lines are also clearly visible in the spectrogram. The line 126 cm.$^{-1}$ is most intense. The line at 46 cm.$^{-1}$ is also fairly intense and sharp. Unfortunately, it falls adjacent to a ghost line at about 60 cm.$^{-1}$ In spite of this, it can be seen as a separate kink in the microphotometer record. The high frequency shift lines at 242 and 287 cm.$^{-1}$ are rather broad, the latter being less intense and more diffuse having a width of about 50 cm.$^{-1}$ Beyond this broad line the intensity falls off abruptly.

Figs. 2 (*a*) and 2 (*b*) represent photographs enlarged to the same extent of the spectrograms taken with the large and medium quartz spectrographs respectively. In spite of the fact that a fairly wide slit had to be used with the larger instrument to get the spectrograms within a reasonable time of exposure, the details of the bromide spectrum are more clearly seen in Fig. 2 (*a*), evidently due to the higher dispersion and resolution of the larger spectrograph. The sharpness and discrete character of some of the Raman

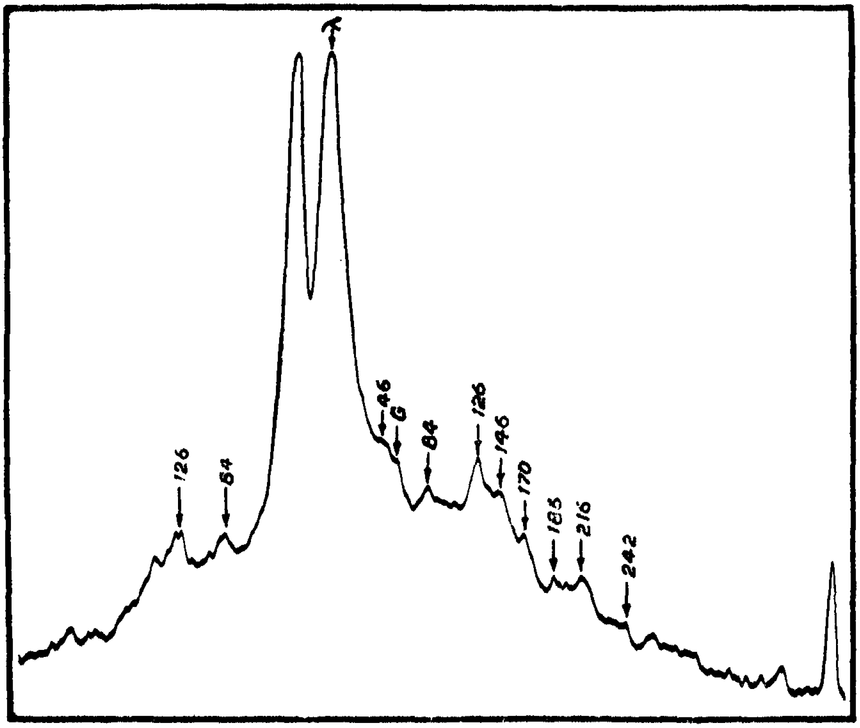

FIG. 3. Microphotometer record of the Raman spectrum of potassium bromide taken with the large quartz spectrograph.

lines are also evident from a scrutiny of the microphotometer record of the spectrogram taken with the large quartz spectrograph reproduced in Fig. 3.

The lines 228 and 232 cm.$^{-1}$ appear as a single line with a mean shift of 230 cm.$^{-1}$ in the photograph taken with the medium quartz spectrograph. In the microphotometer record of the spectrogram taken with the larger quartz spectrograph (Fig. 3) the doublet nature could be easily identified. The width of the line at 186 cm.$^{-1}$ is partly due to presence of a mercury line separated from λ 2536·5 radiation by about 184 cm.$^{-1}$

Fig. 2 (*c*) represents the spectrum of rock-salt taken with the large quartz spectrograph and a fine slit and enlarged to the same extent as Fig. 2 (*a*). It is interesting to note that the discrete character of the second-order spectrum is more clearly evident in the case of potassium bromide than in the case of rock-salt. In the case of the latter, only one line at 235 cm.$^{-1}$ stands out very prominently while in the case of the former, no less than five lines, *viz.*, 84, 126, 146, 170 and 216 cm.$^{-1}$ appear conspicuously. In spite of the smaller values of the frequency shifts in potassium bromide, the lines do not appear bunched up as in sodium chloride, but are evenly distributed over the entire spectrum. Photographs of the Raman spectra of NaCl and KBr taken under comparable conditions with the aid of the medium quartz spectrograph suggested that the scattering power of KBr is greater than that of NaCl.

4. DISCUSSION

Crystal structures of the rock-salt type contain two interpenetrating face-centred cubic lattices. The unit cell is a rhombohedron with one metallic ion and one halogen ion contained in it. According to the new lattice dynamics, of the 48 degrees of freedom, 45 will appear as the atomic frequencies. These 45 frequencies would be reduced by degeneracy to 9 modes with distinct frequencies ν_1 to ν_9. The detailed description of these modes are given in Table I. The expressions for the frequencies of these modes as worked out by K. G. Ramanathan (1947) using only four force constants P, P′, T, T′ are also included in the table. P and P′ represent the forces arising from unit displacements respectively of the two types of atoms in the structure from their positions of equilibrium, while T and T′ represent the forces on a given atom due to a unit displacement of a neighbouring atom of the same kind. The undashed quantities refer to the ions of mass m_1 and dashed ones to ions of mass m_2; $P + 8T = P' + 8T'$. The descriptions of the modes given in Table I are determined only by the crystal structure and are independent of the masses of constituent ions and of the nature of the forces in the crystalline medium. If m_1 and m_2 are the masses of the

TABLE I

The Eigenvibrations of the Rock-salt Structure

Descending Sequence of Frequency	Symbol	Degen-	Oscillating unit	Direction of motion	$4\pi^2\nu^2c^2$	Detailed description
I	ν_1	3	Cubic planes	Normal	$\frac{P-8T}{m_1}+\frac{P'+8T'}{m_2}+\frac{16(T+T')}{m_1+m_2}$	K and Br ions moving in the same phase
II	ν_2	6	Cubic planes	Tangential	$\frac{P}{m_1}+\frac{P'}{m_2}+\frac{8(T+T')}{m_1+m_2}$	K and Br ions moving in opposite phases
III	ν_3	3	Two lattices	Arbitrary	$\frac{P+8T}{m_1}+\frac{P'+8T'}{m_2}$	K and Br ions moving in opposite phases
IV	ν_4	4	Octahedral planes	Normal	$\frac{P-8T}{m_1}$	K ions moving and the Br ions at rest
V	ν_5	8	Octahedral planes	Tangential	$\frac{P+4T}{m_1}$	K ions moving and Br ions at rest
VI	ν_6	4	Octahedral planes	Normal	$\frac{P'+8T'}{m_2}$	K ions at rest and Br ions moving
VII	ν_7	8	Octahedral planes	Tangential	$\frac{P'+4T'}{m_2}$	K ions at rest and Br ions moving
VIII	ν_8	3	Cubic planes	Normal	$-\frac{16(T+T')}{m_1+m_2}$	K and Br ions in opposite phases
IX	ν_9	6	Cubic planes	Tangential	$-\frac{8(T+T')}{m_1+m_2}$	K and Br ions in the same phases

lighter and heavier ions respectively and P, $P' \gg T, T'$, Sir C. V. Raman (1947) has shown that the nine eigenvibrations arrange themselves in descending sequence of frequency in the order indicated in Table I. Before considering the case of potassium bromide in detail, it is useful to discuss the general features of the spectra of different alkali halides possessing the rock-salt structure.

Because of the high symmetry of the structure, all the nine modes will be inactive in the first order Raman effect. In the second-order Raman spectrum, the 9 octaves and 36 combinations of the primary vibration frequencies are allowed to appear. In any particular case, only the octaves and a few combinations may be expected to appear in the spectrum with any appreciable intensity. The actual magnitude of the frequency shifts and their distribution in the spectrum will be determined by the absolute and relative values of the masses of the two kinds of ions. As is to be expected, if the ions are of low atomic weight as in LiF, the frequencies will be high and conversely if the ions are heavy the frequencies will be low. If the ratio of the masses of the cation and the anion is large, the frequencies of nine modes will be such that in the resulting second-order spectrum the Raman lines would be more evenly distributed, thus enabling the discrete character of the spectrum to be exhibited quite clearly. As the ratio of the masses is progressively decreased, the majority of the modes will have frequencies slightly different from one another and the Raman lines appear bunched together over a narrow region of frequency shifts. These conclusions are fully substantiated by the results obtained with KBr and NaCl. As the ratio of the masses of K and Br ions is greater than the ratio of Na and Cl ions, the details of the spectrum are more clearly evident in the case of KBr than in the case of NaCl [see Figs 2 (*a*) and 2 (*c*)]. If the ratio of the masses is nearly unity, *i.e.*, if $m_1 \sim m_2$ as in NaF, KCl and RbBr, the frequencies of some of the pairs of modes become identical, resulting in a perturbation of the vibrational modes. The resulting spectrum will be a complicated one. This aspect of the problem will be discussed in greater detail in a forthcoming paper on the Raman spectrum of potassium chloride.

5. CASE OF POTASSIUM BROMIDE

The nine eigenfrequencies of potassium bromide can be calculated to a first approximation with two assumed force constants only. P = P′ and T = T′. For the alkali halides P is nearly fifty times T. The force constants, for KBr may be expected to be smaller than those for NaCl and KCl (C. V. Raman, 1947). Taking P = $2 \cdot 2 \times 10^4$ dynes/cm. and T = $-\,0 \cdot 034 \times 10^4$ dynes/cm., the frequencies have been evaluated and the values are given in Table II.

TABLE II

Eigenfrequencies of KBr

Mode	$4\pi^2\nu^2c^2$	Calculated frequency cm.$^{-1}$	Observed frequency cm.$^{-1}$
ν_1	$\frac{P-8T}{\mu}+\frac{32T}{m_1+m_2}$	121	121
ν_2	$\frac{P}{\mu}+\frac{16T}{m_1+m_2}$	117	116
ν_3	$\frac{P+8T}{\mu}$	112	114
ν_4	$\frac{P-8T}{m_1}$	104	108
ν_5	$\frac{P+4T}{m_1}$	95	93
ν_6	$\frac{P-8T}{m_2}$	73	73
ν_7	$\frac{P+4T}{m_2}$	67	63
ν_9	$-32T/(m_1+m_2)$	40	42
ν_8	$-16T/(m_1+m_2)$	28	23

As already indicated above, the nine eigenvibrations are inactive in the Raman effect to a first approximation. The frequency shifts recorded in the spectrum should therefore be identified as the octaves and some of the combinations of the eigenvibrations. The octaves are generally more intense than the combinations. Taking this as well as the relationships between ν_4 and ν_6, ν_5 and ν_7 and ν_8 and ν_9 (see Table I), into consideration, the observed frequency shifts 242, 232, 228, 216, 186, 146, 126, 84 and 46 cm.$^{-1}$ have been assigned as octaves of ν_1, ν_2, ν_3, ν_4, ν_5, ν_6, ν_7, ν_8 and ν_9. The observed values for the eigenfrequencies are entered in the last column of Table II. The agreement between the observed and calculated frequencies is satisfactory. The line at 170 cm.$^{-1}$ may be identified as a combination of ν_4 and ν_7. The diffuse and faint band at 287 cm.$^{-1}$ may belong to the third-order spectrum.

The modes ν_4 and ν_5 represent oscillations of the K ions only lying in the octahedral planes, while modes ν_6 and ν_7 represent similar oscillations of the Br ions only. In the normal modes, ν_4 and ν_6, six ions of one kind simultaneously approach or recede from an ion of the other kind, while in the tangential modes, *viz.*, ν_5 and ν_7, two ions of one kind approach, two recede and two others remain at the same distance. Hence the changes of polarisability should be much larger in the normal modes ν_4 and ν_6 than in the tangential modes ν_5 and ν_7. It follows, therefore, that ν_4 and ν_6 should show much stronger activity in the second-order Raman effect than ν_5 and ν_7 respectively. Experimentally it is found that octave of ν_4 (216 cm.$^{-1}$) is more intense than the octave of ν_5 (186 cm.$^{-1}$), while the octave of ν_6 (146 cm.$^{-1}$) is less intense than that of ν_7 (126 cm.$^{-1}$). The abnormally high intensity of the 126 cm.$^{-1}$ line may be attributed to the fact that the combination of ν_4 and ν_9 falls roughly on the octave of ν_7. Since the refractivity of the Br ions is very much larger than that of the K ions, the octaves of modes ν_6 and ν_7 may be expected to appear with greater intensity than the octaves of the corresponding modes ν_4 and ν_5. Indeed, the octaves of ν_6 and ν_7, *viz.*, 146 and 126 cm.$^{-1}$, would be the most intense lines in the spectrum. This is what is actually observed. See Fig. 1.

In modes ν_1, ν_2 and ν_3, the movements of the K and Br ions are similar, the two Br ions on each side of a K ion along the cube axis respectively approaching and receding from it, while the two K ions on each side of a Br ion behave similarly with respect to the latter. Each pair of neighbouring K and Br ions at the phase of their nearest approach would have polarisability greater than the value averaged over the whole period, thus giving rise to scattered radiations of double frequency. Therefore, modes ν_1, ν_2

and ν_8 would be active more or less to the same extent and their octaves would have nearly the same intensity. This conclusion is also supported by facts.

6. THE INFRA-RED ABSORPTION SPECTRUM

The infra-red absorption spectrum of thin films of potassium bromide has been investigated by Barnes (1932). The principal absorption peak was located at $88 \cdot 3 \pm 0 \cdot 5\,\mu$ (113 wavenumbers). Besides this, the existence of one other subsidiary maximum at about $82\,\mu$ (122 wavenumbers) has been established.

Since the two interpenetrating lattices in the structure of potassium bromide consist of dissimilar particles, their oscillation against each other, *viz.*, mode ν_3 in Table I is necessarily active in infra-red absorption. The frequency of the principal infra-red absorption maximum agrees very well with the calculated value for ν_3 (see Table II). In all the other eight eigenvibrations, the phase of the motion is reversed at each successive layer, and hence if they are regarded as independent normal vibrations of the structure they should be inactive in respect of infra-red absorption. But, as has been shown by Sir C. V. Raman, owing to the anharmonicity and the finite amplitudes of oscillation, there would be sufficient coupling between the different modes to make some of the fundamentals or combinations having frequencies near about the frequency of ν_3 active in infra-red absorption. This would explain the broad character of the principal infra-red absorption maximum at $88 \cdot 3\,\mu$ (113 cm.$^{-1}$) and also the appearance of a subsidiary infra-red maximum at about $82\,\mu$ (122 cm.$^{-1}$) corresponding to the intense Raman line at 126 cm.$^{-1}$

7. SUMMARY

The physical basis for the derivation of the result that any crystal has only $24p-3$ normal modes of atomic vibration, p being the number of non-equivalent atoms in the unit cell, has been briefly reviewed. The difficulties connected with the successful recording and interpretation of the spectra of the alkali halides have been pointed out. The Raman spectrum of potassium bromide excited by $\lambda\,2536 \cdot 5$ radiation has been recorded, using both moderate and high dispersion spectrographs. It exhibits a series of sharp Raman lines, eleven of which could be easily identified. The five most intense lines which stand out prominently in the spectrum on account of their extreme sharpness have frequency shifts 84, 126, 146, 170 and 216 cm.$^{-1}$ The numerical evaluation of the nine eigenfrequencies for KBr on the basis of the new lattice dynamics leads to results in good agreement with observational data. Their activities in light-scattering and infra-red absorption are also discussed. The vibrations which are most active in Raman effect are those in which the Br ions lying in the octahedral layers alone move. This result is in general agreement with the observed facts.

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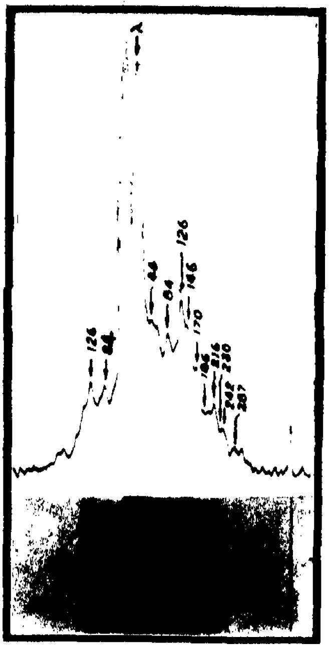

FIG. 1. The Raman spectrum of potassium bromide taken with the medium quartz spectrograph and its microphotometer record.

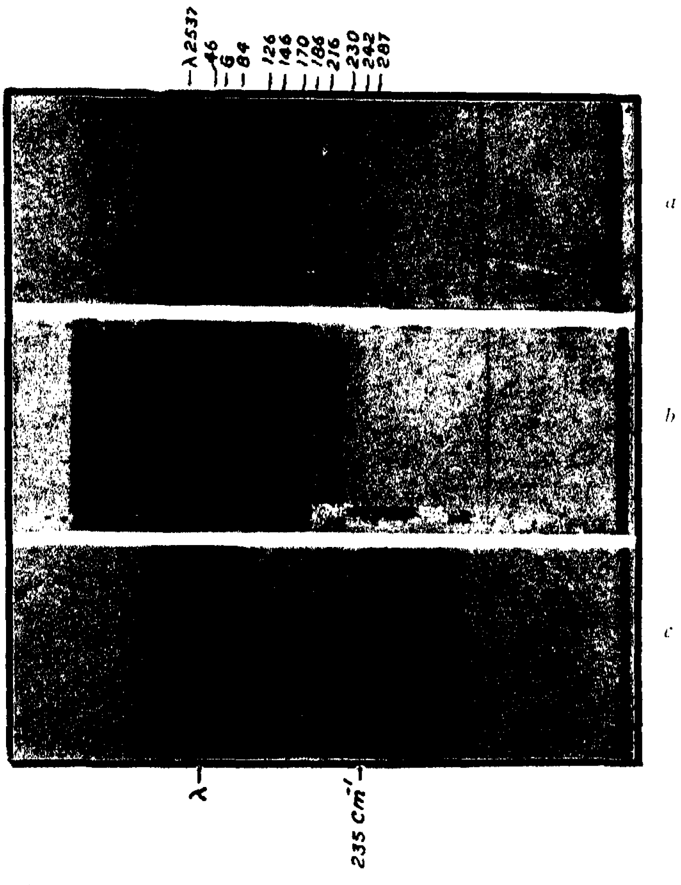

FIG. 2. (*a*) The Raman spectrum of KBr taken with the large quartz spectrograph.
(*b*) The Raman spectrum of KBr taken with the medium quartz spectrograph and enlarged to the same extent as (*a*).
(*c*) The Raman spectrum of NaCl taken with the large spectrograph.

(2) *The extent of the spectrum in the region of high frequency shifts.*— The theoretical curve extends over a region of frequency shifts 1700 to 2700 cm.$^{-1}$, *i.e.*, 1000 wavenumbers. The observed second-order spectrum, on the other hand, is restricted to a region of frequency shifts 2176 cm.$^{-1}$ to 2665 cm.$^{-1}$ Below 2176 cm.$^{-1}$ there is only one faint line at 2015 cm.$^{-1}$ but no continuum of even 1/10th intensity of the 2176 cm.$^{-1}$ line. The extension of the spectrum up to about 1700 cm.$^{-1}$ on the shorter wavelength side, of the type and of comparable intensity as suggested by the theory does not find experimental support.

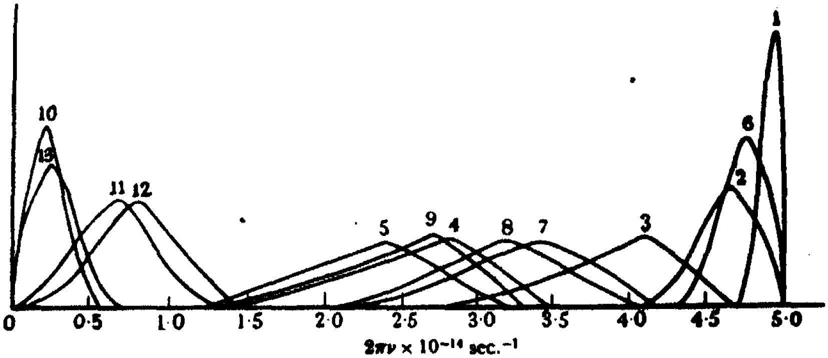

FIG. 1. Frequency density functions $Z^{jj}(\omega)$ taken from Smith's paper.

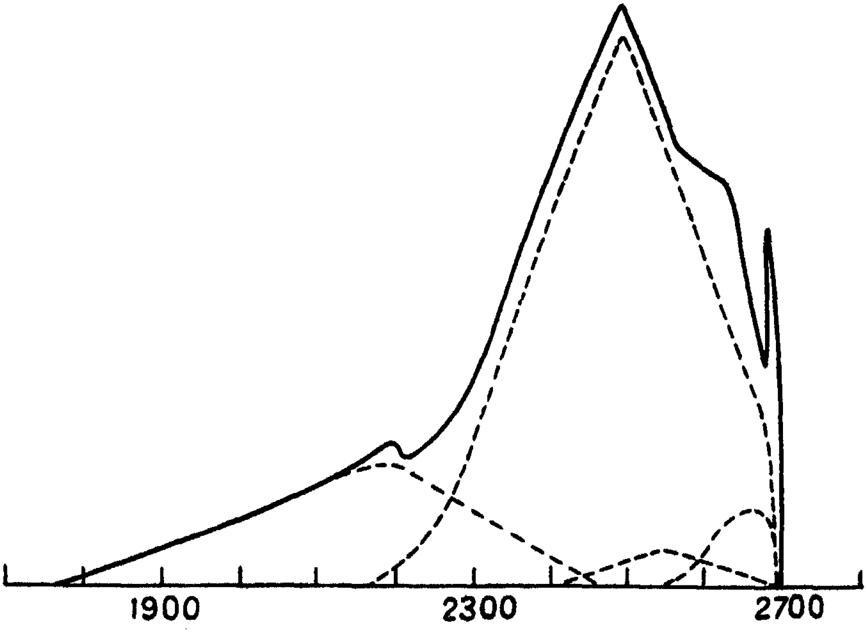

FIG. 2 *a*. The theoretical intensity distribution curve.

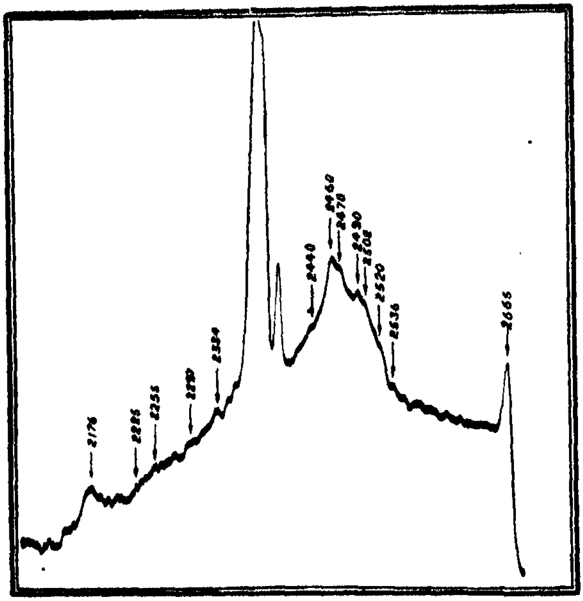

FIG. 2 *b*. Microphotometer record of the second-order Raman spectrum of diamond taken with large quartz spectrograph.

(3) *The number of lines or peaks.*—The theoretical curve exhibits four maxima, as is to be expected by the superposition of the four branches (1), (2), (3) and (6). Any further refinement in the theoretical calculations cannot give rise to more than four maxima in the region under consideration. The microphotometer record of the observed spectrum shows no less than 12 kinks, each one of them representing a sharply defined line. That these kinks are not due to random fluctuations in intensity as Smith would like to call them, will be obvious to anybody who examines the spectrograms taken under high dispersion and resolution. Even a lightly exposed spectrogram reproduced in Fig. 3 exhibits at least four extremely sharp lines adjacent to the most intense line at 2460 cm.$^{-1}$ The theoretical curve has, instead, only one maximum in this region.

(4) *The high frequency cut-off of the spectrum.*—In the intensity distribution curve calculated on the basis of the Born theory, the peak with the maximum frequency shift, *i.e.*, 2664 cm.$^{-1}$ does not coincide with the end of the spectrum, whereas in the experimental curve the line at 2665·4 cm.$^{-1}$ represents the upper limit of the spectrum. This line is the octave of the fundamental mode of oscillation of the diamond lattice having the highest frequency shift, namely 1332 cm.$^{-1}$ As is to be expected, the octave appears as a sharp line and stands out from the rest of the spectrum. The sharp

peak at 2664 cm.$^{-1}$ of the theoretical curve, on the other hand, appears to have been manufactured by giving suitable intensities to the branches (1) and (6).

(5) *Region of low frequency shifts.*—According to the calculations of Smith, the branch (10) (see Fig. 1) has an intensity comparable to that of the high frequency branches and a maximum at 106 cm.$^{-1}$ She says that this low frequency band is not observed experimentally as it may be covered by the incident mercury line. Heavily exposed spectrograms taken with efficient filtering of the exciting radiation do not exhibit any low frequency shift line even faintly, much less a band of the type predicted by the Born theory, other than the Brillouin components. Spectrograms reproduced on page 230 of *Nature* (1947, **160**) and on Plate X of the *Proceedings of the Indian Academy of Sciences* (1947, **26**) will bear testimony to the above statement.

From what has been said above, it is clear that the theoretical intensity curve for the second-order Raman spectrum of diamond is wholly artificial and bears no resemblance whatsoever to the facts. Any theory which wants to hold on its own should be capable of explaining the existence of at least the five sharp intense lines (see Fig. 3), appearing in the second-order spectrum of diamond, not to say anything about the rest. The Born theory as worked out by Smith for the case of diamond, however, is unable to explain them.

In conclusion, the author feels it necessary to refer to some points concerning the theoretical paper by Helen Smith. The experimental results mentioned above were first published in two notes in the correspondence columns of *Nature* in the January 11th and August 16th (1947) issues. In the first note on the " Raman spectrum of diamond under high dispersion ", the spectrograms taken with the large quartz spectrograph and exhibiting the true nature of the Raman spectrum of diamond unambiguously were reproduced. Anyone familiar with the elements of spectroscopy would unhesitatingly admit that the characteristic feature of the spectrum as revealed by the reproduced photographs is the appearance of a whole series of sharply defined Raman lines clearly resolved from one another, a fact which does not find any explanation whatsoever on the Born theory. In the second note on the " Second-order Raman spectra of crystals ", it was clearly pointed out that in spectrograms heavily exposed under the most perfect experimental conditions, there is not a trace of any scattered radiations having frequency shifts (other than the Brillouin doublets) less than 1332 cm.$^{-1}$ The two notes mentioned were published long before Prof. Born

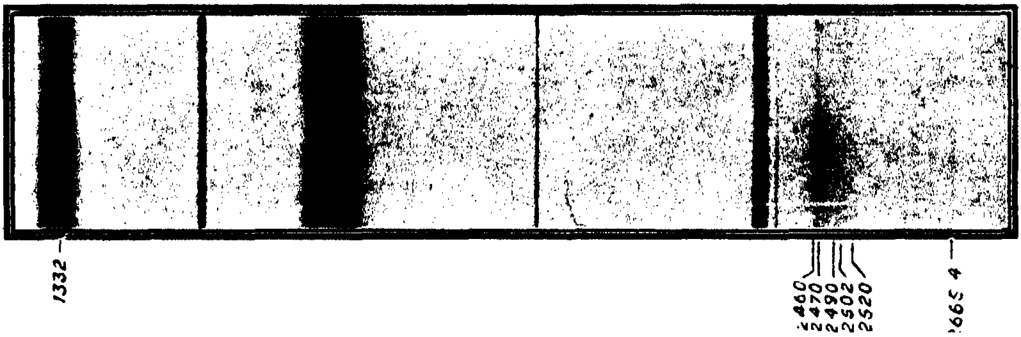

FIG. 3. Lightly exposed photograph of the Raman spectrum of diamond taken with the large quartz spectrograph

communicated the manuscript of Smith's paper to the Royal Society. No reference to them, however, is made in Helen Smith's paper as published.

The detailed paper giving the latest results and a full theoretical discussion appeared in the December (1947) issue of the *Proceedings of the Indian Academy of Sciences*, which would have been received by Prof. Born in the normal course in January or February, 1948. Moreover, the author understands that when Prof. Born presented Smith's theoretical intensity distribution curve during the Bordeaux meeting in April, 1948, he was appraised of the latest experimental results and slides exhibiting them were shown. This took place long before Smith's paper was actually published in the *Transactions of the Royal Society*. It is therefore extremely surprising to find no reference to the author's detailed publication and no attempt to correct the wholly misleading and erroneous statements concerning the experimental facts appearing in Helen Smith's paper.

SUMMARY

The observed features of the Raman spectrum of diamond have briefly been summarised and compared with the theoretical conclusions arrived at by Helen Smith on the basis of Born's postulate of the cyclic lattice. In every respect and especially as regards the form, the extent, the number and sharpness of the lines, the spectrum in the low frequency shift region, etc., the theoretical intensity distribution curve is found to differ widely from what has been observed experimentally. It has been shown that the Born theory as worked out by Smith for the case of diamond is unable to explain the characteristic features of the second-order spectrum of diamond.

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SOME NEW TECHNIQUES IN X-RAY DIFFRACTION

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X-Ray diffraction since the original experiment of von Laue has done much —but it has yet much to do. It is a respected branch of science but it depends for much of its future development on the production of new tools to collect the necessary experimental data, the acquiring of new skills in their use and the development of new arts in the interpretation of the data. We have to-day cameras which permit of the determination of lattice constants to one part in fifty thousand, single crystal cameras which photograph the reciprocal lattice, Geiger counter units which automatically record powder diffraction data and computing machines which take much of the toil from the computation of Fourier series and the determination of crystal structures. What shall we plan now?

A part of the program in our X-ray laboratory is devoted to the development of new instruments. In this brief paper, the program is outlined. Some of the ideas will doubtlessly prove bad—others may prove useful but if they suggest new approaches, then this rather speculative paper will have been justified.

A. Micro Camera Techniques

X-ray scattering gives information concerning the structure of the volume of specimen irradiated by the X-ray beam. The usual techniques employ X-ray beams of the order of a millimetre in cross-section, and so any structural information derived from the study of scattered radiation will be an average of a volume of the order of a cubic millimetre. Many research workers are concerned with structure differentiation on a smaller scale—for this reason the biologist uses the microscope. It has occurred to many workers[1, 2] that the use of finer beams would permit the systematic exploration of specimens by X-ray diffraction on a microscopic scale. The use of fine glass capillaries to define such beams has permitted the construction and use of transmission-cameras using beams as small as 10 microns in cross section. The design[3] of these cameras permits mounting the specimen in the X-ray beam under an optical microscope so that one knows exactly what part of the specimen is in the X-ray beam. The applications of such an instrument are wide.

Thus the biologist can often differentiate structures under the microscope but be unable to identify them. This is particularly true in pathological tissues and yet many biological structures can give distinctive X-ray diagrams. Micro camera techniques seem an answer to this problem.

One need not stop here. A back reflection micro camera has been constructed* and is now being tested. It is hoped to use this instrument in the study of single grains in metals and of intergranular material.

Many biological tissues give significant scattering at very small angles. A small angle micro camera may prove helpful in such studies.

It is usually necessary to have single crystal X-ray data to work out complete structure determination. One can work with very small crystals to-day; crystals as small as 1/20 mm. in the largest direction have been successfully used. This appears to be a lower limit to what can be done with conventional slit systems as the air scattering of the comparatively large X-ray beams approaches the crystal scattering in magnitude. A single crystal micro camera should make possible studies of very much smaller single crystals.

B. SPECTROMETERS

(AUTOMATIC RECORDERS OF POWDER DIFFRACTION DATA)

There are available commercially to-day two somewhat similar (in principle) spectrometers.[5, 4] These use a focussing principle and depend for their resolution on the fine slits (or X-ray focal spots) employed. In theory one can get as high resolution as one wants by narrowing the slits and by obeying very accurately the focussing conditions but in practice it does not work out so easily.

Again many workers have suggested the use of plane crystals[6] and bent crystals[7] for achieving adequate resolving power. The writer suggests that a spectrometer of high resolving power could be constructed using essentially a double plane crystal spectrometer with a scatterer between the crystals. The first crystal could have incident on it at the Bragg angle for the characteristic K radiation a very broad beam of X-rays from a large area focal spot. This incident beam could be slightly collimated by a gross Soller slit arrangement so that the Kβ is not reflected. The broad reflected monochromatic beam would then be incident on a plane surface of a powder specimen set up on an axis of rotation (as in the present spectrometers). Rotating on an arm about the same axis but at twice the angular velocity would be the second plane crystal set to make the Bragg angle for the radiation used with scatttered beams travelling in the direction of the arm. A *wide* window Geiger counter tube mounted on the same arm would be set to receive the radiation reflected by this second crystal. This instrument would have no limiting slits, the angles over which the single crystals used reflect X-rays would in effect be the factors deciding its potential resolving power.

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* The back reflection microcamera was constructed by J. Singer,

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One sometimes wishes to detect and study crystalline impurities in a crystalline matrix. Often the faint lines of the impurity are lost in the more intense pattern of the matrix. A similar problem exists in infra-red work where the lines of a solute are swamped in the pattern of a solvent. The balanced split beam infra-red spectrometer has been of great help and its success suggests that a similar instrument could be constructed for X-ray work. We are attempting to construct such an instrument. The X-ray beam emergent from one window of a tube is split by a horizontal diaphragm. The split beams then enter a similarly bifurcated conventional spectrometer[4] and the reflected beams are received by two Geiger tubes in one glass envelope. The outputs are balanced and the difference is fed into a recorder. Acceptable balancing has not as yet been achieved.

C. LOW TEMPERATURE CAMERAS

Recently we have had occasion to study the structure of cyclooctatetræne.[8] This substance is liquid at room temperatures and X-ray studies, both powder and single crystal, had to be done at below room temperatures. A literature search revealed a dearth of work in this field. Apparently, a few workers had, at one time or another, wanted to study with X-rays, materials not solid at room temperatures and had devised comparatively primitive techniques for doing the job in question. We did the same sort of thing for cyclooctatetræne but because of our experiences realized that a systematic development of low temperature cameras is necessary. Only then can the vast number of simple but important compounds which are crystalline only at low temperatures be properly investigated. We are therefore experimenting with three types of low temperature cameras, namely, single crystal, powder and spectrometer type cameras.

Many rather involved types of cameras have been tried but interestingly enough, for each type, the latest model has been the simplest to construct, the easiest to use and has given the best results. It is already evident that here there is a vast important field waiting to be explored.

These few examples of proposed new X-ray techniques are of course only illustrative of what is needed. X-ray scattering gives evidence of structure and structure is fundamental to so many fields of inquiry which X-rays have not as yet touched. An extensive instrumental development is clearly called for.

Sir C. V. Raman himself in much of his work has given us beautiful new tools to work with, tools which have extended the horizons in many diverse fields of science. This paper is contributed as a tribute to a true prophet of science.

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THE DYNAMIC X-RAY REFLECTIONS IN CARBON SILICIDE

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1. Introduction

Though it has been known for a long time that well-exposed Laue photographs show additional streaks or spots which are not explicable as regular reflections from the crystal planes, the theoretical significance of the phenomenon was first clearly elucidated in the publications of Sir C. V. Raman on the subject in *Current Science* (1940), and *Proceedings of the Indian Academy of Sciences* (1940, 1941). The analysis of the experimental facts observed with diamond (Raman and Nilakantan, 1940–41) revealed three important features of the phenomenon, namely, (1) that it is intimately connected with the dynamics of the crystal, (2) that it is accompanied by a change of frequency, and (3) that it is essentially in the nature of reflections of X-rays by dynamic stratifications in the medium. Further studies of the subject showed that the frequencies of vibration operative in the production of the additional reflections are those of the monochromatic eigenvibrations of the crystal structure excited by the incident X-rays. Besides such reflections, the theoretical treatment also predicts diffuse maxima due to the scattering by the elastic vibrations of the crystal having the largest amplitude. An intensive study of the problem which was stimulated by these publications has led to a clarification of the fundamental ideas regarding the physical nature of these reflections and the vibration spectrum of the crystal lattice.

While it has been conceded by all theorists and experimenters working in the field that the three basic ideas outlined by Raman are essentially valid, there exists some difference of opinion regarding the frequency (or wavelength) region, which is responsible for the observed X-ray effects. According to Born (1941) and his school, the effective wavelengths giving rise to the spot are only the longest in the elastic vibrational spectrum of the crystal. This conclusion is a direct consequence of the hypothesis of Debye, and Born and Karman that the vibrations of a crystal lattice are *non-degenerate* (or single) and distributed over a wide range of frequency. Following Ott

(1935), Born (1942) has also shown that the effect of the type visualised by Raman's theory is theoretically possible, but he *believes* that the intensity of such modified Raman reflections will be extremely small, as the probability of such transitions taking place is not great.

The defect in the argument of Born consists in his assumption that the vibrations in the higher part of the frequency range—the so-called optical series—are non-degenerate in the same manner as the elastic vibrations. By his analysis of the problem which is supported by the experimental spectroscopic facts, Sir C. V. Raman (1943, 1947) has shown that the units of the vibration pattern in crystals are supercells having twice the linear dimensions and therefore eight times the volume of the static units of the crystal structure. The vibrations of the supercell are closely analogous to those of a poly-atomic molecule with the appropriate symmetries, but with this important difference that the atoms in the unit cell are not isolated from the rest of the crystal. There are $(24p-3)$ eigen-vibrations for such a super-cell, where p is the number of atoms in the unit cell. Each of the eigen-vibrations of the super-cell is truly monochromatic and N-fold degenerate, if N is the number of the supercells contained in the crystal. This degeneracy is further increased by virtue of the symmetry of the crystal and is a maximum for cubic crystals. Born's assumption that the lattice vibrations of high frequency are non-degenerate is thus physically untenable, and his objection against the modified X-ray reflections caused by them being sufficiently intense for observation has therefore no theoretical justification. On the other hand, on account of the very high degeneracy of these vibrations one should expect the Raman X-ray reflections caused by them to appear with appreciable intensity. In the above description, a small residue of three degrees of freedom of translation for every supercell appears on ultimate analysis as elastic vibrations having a frequency distribution of the type envisaged by Debye. These elastic waves could be treated as thermal waves which come under the treatment of Faxen (1923) and Waller (1923). The refinement of the latter's theory by Born and Sarginson (1941) leads to a modified expression for the intensity of thermal scattering, and its distribution in terms of the elastic constants of the crystal.

The Raman X-ray reflections are characterised principally by their sharpness and a temperature effect on intensity depending on the eigen-frequency of the lattice vibration but not on the angle of mis-setting of the crystal. The thermal scattering, on the other hand, is characterised by a weak diffuse maximum and a temperature effect whose magnitude depends on the characteristic temperature and on the difference between the glancing angle and the correct Bragg angle of the crystal. In the vast majority of crystals studied, *e.g.*, rock-salt, sylvine, metals, organic crystals, etc., the modified X-ray reflections due to eigen-vibrations and elastic vibrations are superposed, and it is not easy to differentiate them by their experimentally observed features. In the case of diamond, however, the thermal scattering is so weak and the Raman reflections are so pronounced that a study of this crystal has enabled Raman and Nilakantan (1940) to prove all the characteristics of the phenomenon uniquely. Born (1942) and Lonsdale (1942), however, have attempted to explain the specific results of diamond on the plea that "it is not a normal crystal" or "that a strain which is cubic in symmetry is inherent in the majority of diamonds". In an article in *Nature*, Sir C. V. Raman (1942) has shown that such hypotheses are devoid of justification.

In the present investigation the author has studied the dynamic X-ray reflections by carbon silicide (carborundum) which has a structure similar to that of diamond and the results are discussed in relation to the current theories of the phenomenon.

2. CRYSTAL STRUCTURE AND LATTICE SPECTRUM OF CARBORUNDUM

The crystal structure of carborundum has been extensively studied by Ott (1925, 1926). He has discovered four different types, three of which are hexagonal and one is cubic. Sommerfeld (1928) has given a fifth one which is also hexagonal. In the present investigation the author has made use of a thin plate of a natural crystal which is bluish-green in transmitted light. The Laue pattern taken with X-rays normal to the plate shows that it belongs to type II, hexagonal (Fig. 1 *a*). The Bravais elementary cell of this type contains six molecules of SiC. Atoms of one kind are bound to those of the other tetrahedrally. The smallest Si–C distance is 1·9 A.U. and those of the other tetrahedrally. The smallest Si–C distance is 1·9 A.U. and the binding between the atoms is non-polar. The axial lengths of the unit cell are $a = 3\cdot 095$, $b = 5\cdot 38$ and $c = 15\cdot 17$ A.U., where c-axis is perpendicular to the cleavage plane. The structure thus bears a close resemblance to the diamond lattice. According to Schaefer and Thomas (1923) this type of carborundum shows only one strong sharp infra-red reflection at 12μ (830 cm.$^{-1}$). This obviously corresponds to an oscillation of silicon against carbon atoms.

3. SPECULAR CHARACTER OF THE DYNAMIC REFLECTIONS

The X-ray generator used in the present investigation was a demountable Coolidge tube with a Mo-anticathode and operated at 45 kilo-volts and a fairly steady milliampereage of 20 m.A. The crystal was mounted with its

(0001) plane vertical. A narrow beam of X-rays limited by a system of lead slits is let fall on the crystal normally to this plane. The film was placed at a distance of 43·5 mm. from the crystal. Figs. 1 *a* and *b* in the accompanying plate illustrate the Laue pattern obtained after an exposure of one hour; Fig. 1 *a* was taken with a wide circular beam and Fig. 1 *b* with a fine slit. It will be seen that all the six spots arising by reflection from ($\bar{2}021$) planes are accompanied by sharp circular modified spots. The extreme sharpness of the latter may be seen from Fig. 1 *b*. As the white radiation in the source was pronounced, the radial streaks are fairly prominent. Much more satisfactory photographs are obtained using a narrow linear slit. Figs. 2 *a–g* are taken with a linear slit for various settings of the crystal.

The outstanding feature in all these photographs is that the dynamic reflection is as sharp as the Laue reflection itself for a range of 4° on either side of the Bragg setting. The intensity of the spot falls off rapidly as the crystal is turned away and almost completely disappears for an angle of 2½° from the latter position. Unlike diamond, however, the modified spot remains more or less in a stationary position for the whole range. Table I gives the measurements of the angular distances of the Laue (θ_i) and the Raman reflections (θ_m) and the lattice spacing d of ($20\bar{2}\bar{1}$) planes calculated according to Raman-Nath (1940) formula both for k_α and k_β radiations of the source. It will be seen that the spacing has nearly a constant value for both the rays and agrees well with the theoretical data.

TABLE I

Carborundum

$20\bar{2}\bar{1}$ reflections $d = 2{\cdot}68$ Å

$M_0k_\alpha = 0{\cdot}708$ Å; $k_\beta = 0{\cdot}620$ Å

$2\theta_i$	$2\theta_m$		d in Å	
	k_α	k_β	k_α	k_β
19° 33′	15° 10′	13° 7′	2·68	2·72
17° 38′	15° 25′	13° 24′	2·64	2·66
16° 24′	15° 10′	13° 7′	2·68	2·72
15° 10′	15° 10′	13° 7′	2·68	2·72
11° 36′	15° 25′	13° 24′	2·64	2·66
8° 30′	15° 10′	13° 7′	2·68	2·72
7°	15° 10′	13° 7′	2·68	2·72

Mean d = 2·69Å

Another interesting feature of the circular spots (Fig. 1 *a*) which is worth mentioning is the fact that the intensity distribution is *annular with a minimum at its centre.* In order to see whether this is the result of each of the spots being a composite of six others situated hexagonally, the experiment was repeated with a fine aperture lead slit (Fig. 1 *b*); but it was not possible to resolve them any further. In the case of linear slits, however, it was observed that each modified line is accompanied on either side by faint close companions (see Fig. 2). It is possible that each of the spots has a fine structure due to the co-existence of six ' phase waves ' similar to three waves in diamond (Pisharoti, 1941).

4. INFLUENCE OF HIGH AND LOW TEMPERATURES

While the geometric character of the modified spot and the rapid fall of intensity with the rotation of the crystal indicate that we are dealing with a modified reflection, investigations of the relative intensities of these reflections at temperatures varying from − 180° C. to 600° C. have yielded decisive results in favour of the Raman's theory. For low temperature work, the technique of high vacuum low-temperature X-ray spectroscopy described in a previous paper (Venkateswaran, 1941) was employed. A linear slit was made use of, instead of a circular one and the relative intensities were determined by varying the time of exposure at the room temperature till its intensity is equal to that at the low or high temperature as judged visually. For high temperatures, the crystal was mounted in a copper block which is heated by a heating coil. The temperature of the crystal was determined by means of a calibrated thermocouple. The crystal was set at different angles and the intensities at various temperatures compared for each setting with that at the room temperature. The results of measurements are given in Tables II and III. Typical photographs taken at 600° C., 300° C., room temperature 30° C. and the liquid-air temperature −180° C. for the same time of exposure are given in Figs. 3 and 4 (Plate).

TABLE II

Low Temperatures

$2\theta_i$	$2\theta_m$	2ϵ	λ in A.U.	$I_{30^\circ}/I_{-180^\circ}$
11° 15′	15° 10′	3° 55′	89	1
11° 54′	,,	3° 16′	94	1
15° 48′	,,	0° 38′	512	1·1
16° 29′	,,	1° 19′	307	1·05
16° 48′	,,	1° 38′	192	1·05
17° 48′	,,	2° 38′	118	1
19° 5′	,,	3° 55′	89	1

TABLE III

High Temperatures

$2\theta_l$	$2\theta_m$	2ϵ	λ in A.U.	$\frac{I_{30}}{I_{300}}$	$\frac{I_{30}}{I_{600}}$
17° 18′	15° 20′	1° 58′	154	1	1·1
17° 46′	15° 10′	2° 36′	118	1·2	1·2
20° 19′	15° 25′	4° 54′	63	1·2	1·4

According to Raman's formula, the intensity of dynamic reflection is proportional to $\frac{e^{h\nu/k_\nu T}+1}{e^{h\nu^*/kT}-1}$, where ν^* is the frequency of the lattice vibration and T is the absolute temperature. If we assume that $\nu^* = 830\,\text{cm.}^{-1}$ given by the infra-red absorption for carborundum (*loc. cit.*), there should not be any pronounced variation of the intensity of the spot for the range of temperature used. The relative intensity between the different temperatures should also be independent of the angular distance ϵ between the Laue spot and the appropriate Bragg position θ_m. These predictions of the theory are fully supported by the experimental facts. It should, however, be mentioned that due to the diminution of the lattice spacing at low temperatures there is a slight increase in the intensity of the spot compared with that at the room temperature. A similar error prevents an accurate estimate of the intensities at the higher temperatures as well.

If on the other hand, we treat the spot as a diffuse scattering of X-rays by the solid elastic waves, according to Born (1942) the maximum intensity at the Bragg position is proportional to Te^{-T/T_0}, where

$$T_0 = \frac{mk\theta^2}{3h^2}\cdot\frac{a^2}{h_1^2+h_2^2+h_3^2}.$$

(T, absolute temperature, m, atomic mass in grams, a, lattice constant in cm., θ, Debye temperature, k, and h, Boltzman and Planck constants, h_1, h_2 and h_3 are the Miller indices of the nearest Bragg reflection.) The characteristic temperature θ for SiC is estimated roughly from the specific heat data and is about 1750. This gives for the (20$\bar{2}$1) plane a value for $T_0 \approx 10^5$. Hence for the temperatures used, the intensity of the diffuse scattering at the Bragg position is nearly proportional to the absolute temperature T. The wavelength λ of the elastic wave effective at each setting of the crystal is calculated according to the approximate relation $\lambda = \frac{d}{\sin\epsilon}$ and given in column 4 of Tables II and III. The thermal theory of diffuse scattering thus leads us to expect that the intensity at the liquid-air temperature should be one-third and those at 300° C. and 60C° C. to be respectively twice and thrice at the room temperature. These relative intensities should also show a dependence on the wavelength of the wave corresponding to the angle of setting of the crystal. Both these conclusions drawn from Born's theory are not supported by the results of the present investigation.

5. CONCLUSION

The main results of the present investigation of the non-Laue spots in the diffraction of X-rays by carborundum may be stated as follows:

1. The modified spots show a hexagonal pattern similar to the Laue spots and are closely related to the internal structure of the crystal.

2. They are sharp for an angular range of nearly 4° on either side of the correct Bragg setting.

3. They are fairly intense near the Bragg position; but the intensity falls off rapidly as the crystal is rotated away from this position.

4. The spots obtained with a circular beam of X-rays have an annular distribution of intensity.

5. The intensity of the modified spot is nearly independent of temperature for all orientations of the crystal.

These results for carborundum are exact parallels to those for diamond. As has been remarked by Sir C. V. Raman (1948) in a recent note in *Nature,* the very fact that the modified spots have a regular geometric pattern bearing an observable relationship to the structure of the crystal is itself a sufficient indication of the connection between them and the eigen-vibrations of the super-cell. The characteristics of the spots enumerated above follow as a necessary consequence of such an origin for these spots.

The above experimental work was carried out in the Physics Laboratory of the Indian Institute of Science, Bangalore, and I desire to place on record my heartfelt gratitude to Sir C. V. Raman for his kind suggestions and inspiring interest in the work.

SUMMARY

Raman's theory of dynamical X-ray reflections and the thermal theory of diffuse X-ray scattering are critically reviewed. An investigation of the extra-spots in X-ray diffraction by the {2021} planes of a hexagonal type of carborundum crystal shows that the spots are sharp and their intensity is nearly independent of temperature for a wide range from − 180° C. to 600° C. and for different orientations of the crystal. It has been shown that they

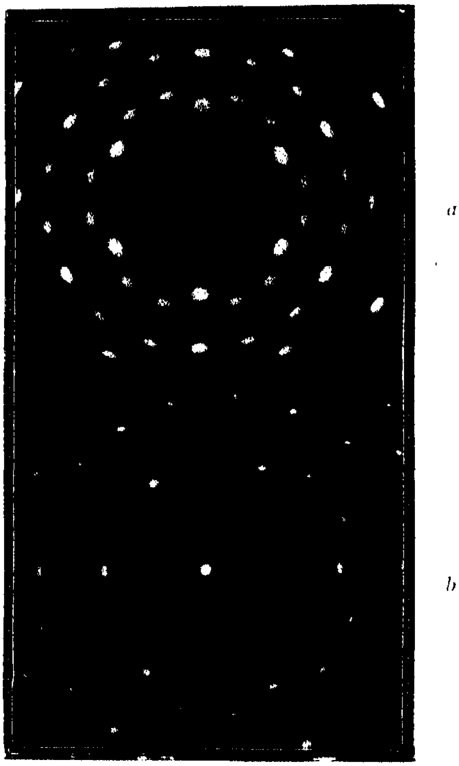

FIG. 1. Carborundum—Laue Photographs
(*a*) Broad Slit. (*b*) Fine Slit

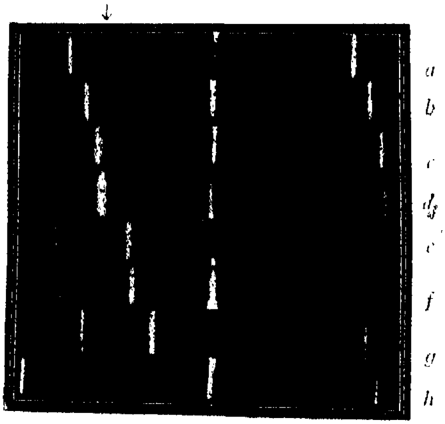

FIG. 2. Carborundum—Orientation Studies

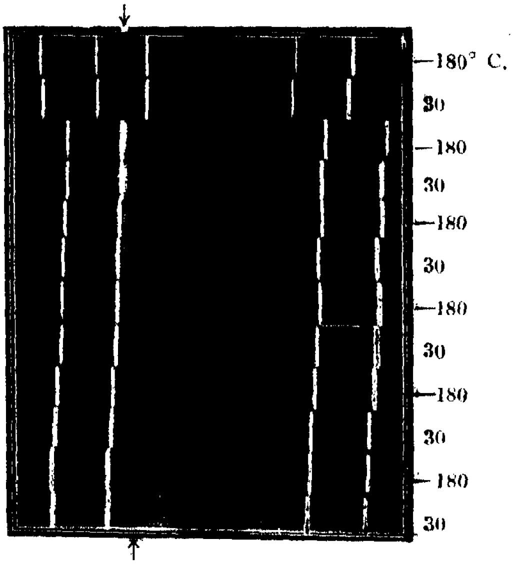

FIG. 3. Carborundum. Low Temperature Studies

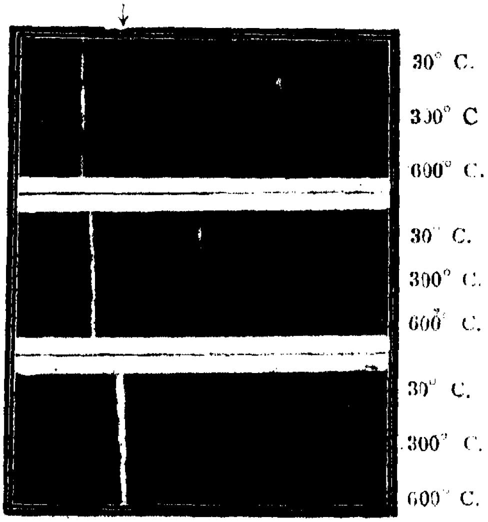

FIG. 4 Carborundum. High Temperature Studies

can be explained as due to the coherent modified reflections of X-rays by the eigen-vibrations of the crystal lattice having a frequency of 830 cm.$^{-1}$ which is observed in the infra-red absorption as well and that the diffuse thermal scattering due to the long elastic waves is not responsible for their appearance.

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FOURIER ASPECTS OF IMPLICATION THEORY

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INTRODUCTION

IT is well known that the electron density of the structure of a crystal at a selection of points with co-ordinates xyz can be determined from the collection of diffraction spectra produced by a crystal, with the aid of the relation

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl}\, e^{2\pi i(hx+ky+lz)} \tag{1}$$

The difficulty with the practical application of this relation is that the diffraction coefficients F_{hkl} are not simple magnitudes, but rather are complex quantities involving both magnitude and phase components. Although the magnitudes of the F's can be determined by experiment, to date there has been no experimental method developed for the determination of their phases. One vehicle for supplying some of these phases or their equivalents is *implication theory*. This has been discussed previously[1] from a group theoretical approach, an approach which has not met with favour in some quarters. In the present communication, a Fourier approach to implication theory is given.

FOURIER DEVELOPMENT OF THE IMPLICATION FUNCTION

In implication theory, use is made of the Patterson function[2]

$$P(uvw) = \frac{1}{V^2} \sum_h \sum_k \sum_l F^2_{hkl}\, e^{2\pi i(hu+kv+lw)} \tag{2}$$

This function has peaks at positions uvw corresponding to locations of all pairs of atoms in (1), such that

$$\begin{aligned} u &= x_2 - x_1 \\ v &= y_2 - y_1 \\ w &= z_2 - z_1, \end{aligned} \tag{3}$$

where the 2's and 1's refer to the two atoms of the pair.

Now, if the crystal has symmetry, there are symmetry relations among the co-ordinates of equivalent atoms, that is, among some of the x's, y's, and

z's of (3). These relations for the operation of a symmetry element parallel to Z are listed in Table I. For these axes, w assumes the limited and characteristic values of 0, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, or $\frac{1}{6}$ only, corresponding with screw operations with translation components 0, $\frac{1}{2}c$, $\frac{1}{3}c$, $\frac{1}{4}c$, or $\frac{1}{6}c$, respectively. For such values of w, characteristic of an operation allowed by the symmetry of the crystal, the designation w_c will be adopted.

If these characteristic values of w_c are substituted into (2), it takes the following, simpler two-dimensional form:

$$P(uvw_c) = \frac{1}{V^2} \sum_h \sum_k C_{hk} e^{2\pi i(hu+kv)}, \tag{4}$$

where values of the Fourier coefficients, fixed for each value of hk, are of the form

$$C_{hk} = \sum_l F^2_{hkl}\, e^{2\pi ilw} . \tag{5}$$

This can be compared with the two-dimensional projection of (1) on the plane (001):

$$\rho(xy) = \frac{1}{A} \sum_h \sum_k F_{hk0}\, e^{2\pi i(hx+ky)} \tag{6}$$

$$P(uvw_c) = \frac{1}{V^2} \sum_h \sum_k C_{hk}\, e^{2\pi i(hu+kv)} \tag{4}$$

These two functions have very similar form. Furthermore, for every peak on (6) there is a corresponding peak on (4), only these peaks are differently placed. In the first case, the peak is at xy, while in the second it is at uv. The question arises, is it possible to refer (4) to different axes such that for each peak on (6), the corresponding peak on (4) has the same co-ordinates, xy? If this can be done, then (4) will perform the same function for the crystal structure analyst as (6).

Now, this transformation can indeed be effected, and in the following way: New axes, $\vec{a}'$ and $\vec{b}'$, are required to replace the old axes, $\vec{a}$ and $\vec{b}$. Furthermore, the fractional co-ordinates, x' and y', along these axes must be equal to u and v. In short, the requirements of the transformation are

$$x'\vec{a}' + y'\vec{b}' = u\vec{a} + v\vec{b}. \tag{7}$$

Table I, column 3, provides the specific values of u and v for the various symmetries. To make clear the use of (7) in finding the required transformation, consider the following specific examples:

For $n = 2$, Table I, column 3, shows that (7) must have the following specific form:

$$x'\vec{a}' + y'\vec{b}' = 2x\vec{a} + 2y\vec{b}. \tag{8}$$

Now, to solve for $\vec{a}'$, let $x' = 1$ and $y' = 0$. Since the purpose of this transformation is that $x' = x\ (= 1)$ and that $y' = y\ (= 0)$, (8) takes the particular form

$$\vec{a}' = 2\vec{a}. \tag{9}$$

To solve for b', let $x' = x = 0$, and $y' = y = 1$. Then the particular form of (8) is

$$\vec{b}' = 2\vec{b} \tag{10}$$

Assembling the information from (9) and (10), the required transformation for $n = 2$ is evidently

$$\begin{aligned} \vec{a}' &= 2\vec{a} \\ \vec{b}' &= 2\vec{b}. \end{aligned} \tag{11}$$

For $n = 3$ (to take another example), Table I, column 3, shows that (7) assumes the specific form

$$x'\vec{a}' = y'\vec{b}' = (x + y)\,\vec{a} + (-x + 2y)\,\vec{b}. \tag{12}$$

To solve for $\vec{a}'$, assume, as before, that $x' = x = 1$, $y' = y = 0$. The particular form of (11) then is

$$\vec{a}' = \vec{a} - \vec{b}. \tag{13}$$

To solve for $\vec{b}'$, next consider $x' = x = 0$, $y' = y = 1$. Then (12) becomes

$$\vec{b}' = \vec{a} + 2\vec{b}, \tag{14}$$

and the entire transformation for $n = 3$ is

$$\begin{aligned} \vec{a}' &= \vec{a} - \vec{b} \\ \vec{b}' &= \vec{a} + 2\vec{b}. \end{aligned} \tag{15}$$

The transformations for these and other symmetries are listed in column 4 of Table I. Now, if an axial transformation is performed on (8), a transformation of indices, $hk \rightarrow h'k'$ also occurs simultaneously. The index transformations are listed in column 5 of Table I.

TABLE I

Symmetry operation. $(n)^p$ indicates the p^{th} power of the operation	Point produced by operation from point at xyz			Patterson uvw for operation			Axial transformation		Index transformation	
							a'	b'	h'	k'
2	$\bar{x}$	$\bar{y}$	z	$2x$	$2y$	0	$2a$	$2b$	$2h$	$2k$
2_1	$\bar{x}$	$\bar{y}$	$z+\frac{1}{2}$	$2x$	$2y$	$\frac{1}{2}$				
3	$\bar{y}$	$x-y$	z	$x+y$	$-x+2y$	0	$a-b$	$a+2b$	$h-k$	$h+2k$
3_1	$\bar{y}$	$x-y$	$z+\frac{1}{3}$	$x+y$	$-x+2y$	$\frac{1}{3}$				
3_2	$\bar{y}$	$x-y$	$z-\frac{1}{3}$	$x+y$	$-x+2y$	$-\frac{1}{3}$				
$(\bar{3})^4 = 3$	$\bar{y}$	$x-y$	z	$x+y$	$-x+2y$	0				
4	$\bar{y}$	x	z	$x+y$	$-x+y$	0	$a-b$	$a+b$	$h-k$	$h+k$
4_1	$\bar{y}$	x	$z+\frac{1}{4}$	$x+y$	$-x+y$	$\frac{1}{4}$				
4_2	$\bar{y}$	x	$z+\frac{1}{2}$	$x+y$	$-x+y$	$\frac{1}{2}$				
4_3	$\bar{y}$	x	$z-\frac{1}{4}$	$x+y$	$-x+y$	$-\frac{1}{4}$				
$(\bar{4})^2 = 2$	$\bar{x}$	$\bar{y}$	z	$2x$	$2y$	0	$2a$	$2b$	$2h$	$2k$
6	$x-y$	x	z	y	$-x+y$	0	$-b$ (equivalent to: a	$a+b$ b)	$-k$ (equivalent to h	$h+k$ k)
6_1	$x-y$	x	$z+\frac{1}{6}$	y	$-x+y$	$\frac{1}{6}$				
6_2	$x-y$	x	$z+\frac{1}{3}$	y	$-x+y$	$\frac{1}{3}$				
6_3	$x-y$	x	$z+\frac{1}{2}$	y	$-x+y$	$\frac{1}{2}$				
6_4	$x-y$	x	$z-\frac{1}{3}$	y	$-x+y$	$-\frac{1}{3}$				
6_5	$x-y$	x	$z-\frac{1}{6}$	y	$-x+y$	$-\frac{1}{6}$				
$(\bar{6})^2 = 3$	$\bar{y}$	$x-y$	z	$x+y$	$-x+2y$	0	$a-b$	$a+2b$	$h-k$	$h+2k$

Since the transformed series (8) has a peak at co-ordinates xy for every peak on (6) at xy, one can infer atom locations from the transformed series. It is therefore called the *implication function.* Let n be the order of the symmetry axis ($n = 2, 3, 4,$ or 6), then the symbol $I_n(xyw_c)$ is used to indicate the transformed series $P(uvw_c)$. Thus, if the operation of transformation is represented by ϕ,

$$I_n(xyw_c) = \phi P(uvw_c) \tag{16}$$

Applying this transformation to (4), it compares with (6) as follows:

$$(6) \qquad \rho(xy) = \frac{1}{A}\sum_h \sum_k F_{hk0}\, e^{2\pi i(hx+ky)} \tag{17}$$

$$I_n(xyw_c) = \frac{1}{V_{\frac{1}{2}}}\sum_{h'}\sum_{k'} C_{h'k'}\, e^{2\pi i(h'x+k'y)} \tag{18}$$

The practical value of (18) can be briefly summarized as follows: It is impossible to make use of (17) directly because the phases of the F's are not known. However, (8) has peaks at the same places, yet does not require a knowledge of the phases of the F's, since the Fourier coefficients, namely, the C's in this case, depend only on F^2's, according to (5). Thus, function (18) may be used as a practical substitute for (17).

IMPLICATION AMBIGUITIES

Unfortunately (18) not only provides peaks at the same locations as (17) but it also contains certain additional peaks as well. These unwanted peaks fall into two classes:

Additional peaks of one variety are known as *satellites*. These arise as a consequence of higher powers of symmetry operations than the first having w_c the same as the first power. Since satellites are dependent on the characteristic symmetry operations, their co-ordinates bear simple geometrical relations to the desired peaks. They can therefore be identified as satellites on this basis.

The other variety of additional peaks are called ambiguities. These arise as a consequence of the transformation of axes which converted (4) into (18). An important feature of this transformation is that h is transformed into h' and k into k'. The transformations occur modulo M, where M has the value of 4, 3, 2, or 1. It follows that all possible values of h' and k' do not occur. Indeed only a fraction, $f = \frac{1}{M}$, of all possible combinations of h' and k' arise. This fraction varies with the order of the symmetry operation of the implication. Let n be the order of axial symmetry. Then the symmetry operation has an angular component $\alpha = \frac{2\pi}{n}$. The fraction of the possible $h'k'$ combinations which are made available through the transformation are then as follows:

n	M	f
2	4	$\frac{1}{4}$
3	3	$\frac{1}{3}$
4	2	$\frac{1}{2}$
6	1	1

The significance of this is that each $h'k'$ combination corresponds to a Fourier coefficient. If only a fraction, f, of the $h'k'$'s are available, only that fraction of the Fourier coefficients are available for forming the implication function (8).

Now, a Fourier series with only a fraction of the coefficients available produces a picture composed of M overlapping images of the crystal structure.

The images are displaced from one another by a translation interval related to the true translations of the crystal by the same transformation which transformed the *hk*'s into *h'k'*'s. In other words, this implies that the implication cell is a submultiple of the true crystal cell. The submultiple aspect is responsible for the overlapping images.

This feature can also be appreciated by reference to reciprocal space as follows: Each available Fourier coefficient corresponds with a point on the reciprocal lattice. A missing coefficient corresponds with a reciprocal lattice point of weight zero, namely a missing point. Thus the reciprocal lattice of the implication has a larger cell than the crystal, and so the direct lattice of the implication must have a smaller cell than the crystal.

Thus, the implication contains a map of the crystal structure plus $M-1$ ghosts of the structure. To wipe out the ghosts, M times as many Fourier coefficients would have to be available.

RESOLUTION OF THE AMBIGUITIES

It is possible to choose between the M possible locations of atoms by the following considerations: In the first place, the ambiguity factor for one symmetrical set of atoms alone has no meaning because it presents no problem. For, any one of the M locations could be chosen arbitrarily as the location of the one atom, and the remaining ones would be known to be ghosts.

The ambiguity factor is only important when there are two or more atoms. The location of the first atom, say A, can then be arbitrarily chosen at one of its M locations on the implication. However, the location of the second atom, B, cannot be determined from the implication without ambiguity. Fortunately, both the three-dimensional Patterson function $P(uvw)$ and its two-dimensional projection, $P(uv)$ contain criteria for distinguishing between the several allowed locations of B, for they both contain peaks for interatomic vectors from A to B, at the co-ordinates

$$uv = (x_B - x_A)\,(y_B - y_A) \tag{19}$$

The implication function contains M peaks for B, namely $x_{B1}\,y_{B1}$, $x_{B2}\,y_{B2}, \ldots$ $x_{BM}\,y_{BM}$. But only one of these values appear in (19) for the Patterson function, and, therefore, with its aid all but one can be eliminated from the implication as ghosts. This elimination method has been successfully used in the writer's laboratory.

To make this elimination, either a three-dimensional Patterson function, or a two-dimensional Patterson function must be computed. The use of the three-dimensional function for this purpose is not only elegant, but it eliminates many possibilities of overlap of peaks, which might otherwise occur in the two-dimensional function, but the labour of computation is great. For many crystal structure purposes, the two-dimensional Patterson function supplies sufficient information for elimination of ghosts, and its computation is much less tedious.

Note that an ambiguity exists for every kind of atom in the crystal except the first atom, designated A above. Therefore, if the crystal is composed of R symmetrically different kinds of atoms, the implication contains $(M-1)(R-1)$ incorrect atom locations. To remove these requires the finding of $R-1$ peaks due to unsymmetrical interactions in the Patterson function.

AMBIGUITIES IN PHASE DETERMINATION

Since (18) has all the peaks contained in (17), plus some additional satellitic peaks, plus some peaks representing ambiguities, it should be possible to find relations between the Fourier coefficients $C_{h'k'}$ and F_{hk0} of these two distributions. The method of finding these relations has been discussed in another place.[3,4] In effect, these relations provide the means of determining the unknown phases of the Fourier coefficients F_{hk0}, provided that the crystal has some kind of axial symmetry.

One of the remarkable features brought out by such relations is that the imaginary component of the phase can be found in the one crystallographic case where it occurs, namely where $n = 3$ (the method fails if $w_c = 0$). To appreciate this, recast (17) and (18) into forms which decompose them into real and imaginary components, *i.e.*, $F = A + iB$, and $e^{i\phi} = \cos\phi + i\sin\phi$. They then become

$$(17): \quad \rho(xy) = \frac{1}{A}\sum_h\sum_k A_{hk0}\cos 2\pi(hx+ky) + B_{hk0}\sin 2\pi(hx+ky) \qquad (20)$$

$$(18): \quad \mathrm{I}_n(xyw_c) = \frac{1}{V^2}\sum_{h'}\sum_{k'} C_{\mathrm{A},h'k'}\cos 2\pi(h'x+k'y) + C_{\mathrm{B},h'k'}\sin 2\pi(h'x+k'y). \qquad (21)$$

The value of $C_{\mathrm{B},h'k'}$, and its reduction for the case of $n = 3$, is as follows:

$$C_{\mathrm{B},h'k'} = \sum_l F^2_{h'k'l}\sin 2\pi\frac{l}{w_c} = \frac{\sqrt{3}}{2}\Big(\sum_{l=3n+1} F^2_{h'k'l} - \sum_{l=3n-1} F^2_{h'k'l}\Big). \qquad (22)$$

Unfortunately, (21) becomes zero either for $w_c = 0$ (which occurs for axes of pure three-fold rotation) or when the space group contains symmetry operations of both the first and second sorts, *i.e.*, when it contains both right and left-handed three-fold screws. In other cases, namely, when the space group contains only three-fold screws of one sense, (21) does not vanish, and then provides the imaginary component of the Fourier coefficients.

Another method of limiting the phases of the F_{hk}'s has been provided by Harker and Casper[5] in the form of inequalities connecting F_{hk}'s with certain $F^2_{h'k'}$'s. These inequalities also involve the same transformed $h'k'$'s as the ones discussed above. Therefore, both the inequalities and the relations discussed above in this section suffer from providing only a fraction of the Fourier coefficients required for the complete electron density summation. They therefore both suffer from the ambiguities discussed above.

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A SIMPLIFIED TREATMENT OF THE DIFFRACTION OF X-RAYS FROM PERTURBED LATTICES

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INTRODUCTION

In this paper it is proposed to present an account of the diffraction of X-rays from perturbed lattices. Certain simplifying assumptions will be made which render the mathematics tractable and, at the same time, are not so much at variance with the true physical picture as to cause violent disagreement with observation.

It should be understood that no attempt is made to decide between the various theories of the basic causes of lattice perturbation; the present treatment is sufficiently general to cover all of these, and forms a means of directly linking any conception of the state of a crystal lattice with the X-ray pattern which it would produce.

2. BASIC ASSUMPTIONS

It is proposed to treat two general kinds of lattice perturbation.

(1) Periodic.

(2) Random.

The former case will be simplified by the following assumption. If a certain cell be chosen as origin the perturbation of any other cell is a periodic function of its position and the perturbation displacements of all the atoms in that particular cell are equal. This is equivalent to treating the cell contents as rigid units.

For the case of random displacements it will be assumed that all cells are in their correct positions but that a particular atom in each cell is displaced from its mean position in such a way that no phase relationship obtains between the displacements of the same atom in different cells.

3. THE CASE OF PERIODIC DISTURBANCE

Classical X-ray crystallography shows that the most general form of the structure factor of an X-ray reflection is given by (1):

$$\left.\begin{aligned} F^2(h, k, l) &= A^2 + B^2 \\ A &= \sum_r f_r \cos \theta_r \\ B &= \sum_r f_r \sin \theta_r \\ \theta_r &= 2\pi \left(h \frac{x_r}{a} + k \frac{y_r}{b} + l \frac{z_r}{c} \right) \end{aligned}\right\} \tag{1}$$

where (h, k, l) are the indices of the plane giving rise to reflection, f_r is the atomic scattering factor of the rth atom in the unit cell (x_r, y_r, z_r) are the co-ordinates of the rth atom and (a, b, c) are the repeat units of the cell.

If now the whole crystal lattice is perturbed in such a manner as to repeat on a superlattice of axes (Ma, Nb, Rc), instead of Bragg reflections occurring only for integral values of (h, k, l) in (1) a new set of reflections will occur in what are effectively fractional values of (h, k, l) as referred to the primitive lattice (a, b, c).

These new reflections can be assigned indices:

$$\left.\begin{aligned} H &= h + \frac{\mu}{M} \\ K &= k + \frac{\nu}{N} \\ L &= l + \frac{\rho}{R} \end{aligned}\right\} \tag{2}$$

where (μ, ν, ρ) are integers which take up all values less than M, N and R respectively.

The perturbation function is defined by:—

$$\left.\begin{aligned} &\Delta_a\,(\alpha, \beta, \gamma) \\ &\Delta_b\,(\alpha, \beta, \gamma) \\ &\Delta_c\,(\alpha, \beta, \gamma) \end{aligned}\right\} \tag{3}$$

such that *all* x co-ordinates in the unit cell located at $(\alpha a, \beta b, \gamma c)$ are displaced by the same amount $\Delta_a(\alpha, \beta, \gamma)$ are similarly for y and z.

Introducing the above notations into equation (1) it is seen that:

$$A\,(H, K, L) = \sum_r f_r \sum_{\alpha=0}^{M-1} \sum_{\beta=0}^{N-1} \sum_{\gamma=0}^{R-1} \cos \left[\theta_r + 2\pi \left\{ \frac{H}{a}\,(a\alpha + \Delta_a) + \frac{K}{b}\,(b\beta + \Delta_b) + \frac{h}{c}\,(c\gamma + \Delta_c) \right\} \right] \tag{4}$$

where Θ_r is the value of θ_r under the substitution $h = \mathrm{H}$, etc.

After some manipulation (4) reduces to:

$$\mathrm{A}\,(\mathrm{H}, \mathrm{K}, \mathrm{L}) = \sigma_c \sum_r f_r \cos \Theta_r - \sigma_s \sum_r f_r \sin \Theta_r$$

and similarly

$$\mathrm{B}\,(\mathrm{H}, \mathrm{K}, \mathrm{L}) = \sigma_s \sum_r f_r \cos \Theta_r + \sigma_c \sum_r f_r \sin \Theta_r \tag{5}$$

where

$$\left.\begin{aligned} \sigma_c &= \sum_{\alpha=0}^{\mathrm{M}-1} \sum_{\beta=0}^{\mathrm{N}-1} \sum_{\gamma=0}^{\mathrm{R}-1} \cos 2\pi \left[\left(\frac{\mu\alpha}{\mathrm{M}} + \frac{\nu\beta}{\mathrm{N}} + \frac{\rho\gamma}{\mathrm{R}}\right) + \left(\frac{\mathrm{H}\Delta_a}{a} + \frac{\mathrm{K}\Delta_b}{b} + \frac{\mathrm{L}\Delta_c}{c}\right)\right] \\ \sigma_s &= \sum_{\alpha=0}^{\mathrm{M}-1} \sum_{\beta=0}^{\mathrm{N}-1} \sum_{\gamma=0}^{\mathrm{R}-1} \sin 2\pi \left[\left(\frac{\mu\alpha}{\mathrm{M}} + \frac{\nu\beta}{\mathrm{N}} + \frac{\rho\gamma}{\mathrm{R}}\right) + \left(\frac{\mathrm{H}\Delta_a}{a} + \frac{\mathrm{K}\Delta_b}{b} + \frac{\mathrm{L}\Delta_c}{c}\right)\right] \end{aligned}\right\} \tag{6}$$

From (1) and (5) the interesting fact emerges that:

$$\mathrm{F}^2\,(\mathrm{H}, \mathrm{K}, \mathrm{L})_{(\text{superlattice})} = (\sigma_c^2 + \sigma_s^2)\, \mathrm{F}^2\,(\mathrm{H}, \mathrm{K}, \mathrm{L})_{(\text{primitive lattice})} \tag{7}$$

which means that the intensity of any superlattice reflection contains as a factor the F^2 value from the primitive lattice considered as being generated by a plane of *fractional indices.*

This result is important as it establishes the validity of phase angle determination methods[2] based on the vanishing of non-Bragg reflections.

In all of the foregoing treatment the perturbation of the lattice has been considered as a static one. Since, however, the frequency of any lattice vibration is very small compared with that of the incident X-ray beam, this assumption will not affect the results. The intensity recorded in a photographic plate will be the time integral of reflections from the lattice. Thus, assuming that the Δ_a, Δ_b, Δ_c are functions of time, the actual recorded intensity is given by:

$$\begin{aligned} \mathrm{I}_{\mathrm{HKL}} &= \mathrm{GF}^2\,(\mathrm{H}, \mathrm{K}, \mathrm{L})_{\text{superlattice}} \\ &= \mathrm{GF}^2\,(\mathrm{H}, \mathrm{K}, \mathrm{L})_{\text{primitive lattice}} \times \int_0^{\mathrm{T}} (\sigma_c^2 + \sigma_s^2)\, dt, \end{aligned} \tag{8}$$

where G is the usual constant involving Lorentz and Polarisation Factors.

Of course, the assumption that the lattice perturbation has wavelengths (Ma, Nb, Rc) can also be generalised but a result of the form of (8) will always obtain, the difference being that, instead of discrete fractional reflections being observed, a continuous background of intensity will be generated due to non-resolution, and this will vanish where F^2 (primitive lattice) is zero.

4. THE CASE OF RANDOM DISTURBANCES

The case of a stationary lattice in which a single atom in each unit cell is executing thermal vibrations will now be considered. It will be assumed that there is no phase relationship between the vibrations of atoms in different cells.

It is easily shown that,[1] if a monochromatic beam of X-rays is incident on the contents of a unit cell, the diffracted beam is given by:

$$\mathcal{A} = \mathrm{A}\sum_{r=1}^{\mathrm{N}} f_r \cos\left[2\pi\left(\frac{t}{\tau}-\frac{x}{\lambda}\right)+\theta_r\right] \tag{9}$$

where

$$\theta_r = 2\pi\left(h\frac{x_r}{a}+k\frac{y_r}{b}+\rho\frac{z_r}{c}\right)^{*} \tag{10}$$

and A is the amplitude of the incident radiation.

Suppose now that the co-ordinates of the sth atom are not exactly (x_s, y_s, z_s) but differ by small quantities

$$\Delta_a^s,\ \Delta_b^s,\ \Delta_c^s. \tag{11}$$

These quantities will vary randomly from cell to cell and, in general, with time.

Substituting from (11) in (9) and (10), neglecting squares and higher powers of the Δ^s and expanding gives:

$$\begin{aligned}\mathcal{A} &= \mathrm{A}\,|\,\mathrm{F}(h,k,l)\,|\cos\left[2\pi\left(\frac{t}{\tau}-\frac{x}{\lambda}\right)+\alpha\right]\\ &\quad -2\pi\mathrm{A}f_s\left(\frac{h}{a}\Delta_a^s+\frac{k}{b}\Delta_b^s+\frac{l}{c}\Delta_c^s\right)\sin\left[2\pi\left(\frac{t}{\tau}-\frac{x}{\lambda}\right)+\theta_s\right]\end{aligned} \tag{12}$$

Now, when all the unit cells of the crystal are considered, the total diffracted intensity is given by:

$$\begin{aligned}\mathcal{A}_{\mathrm{T}} = \Sigma\mathcal{A} &= \mathrm{A}\,|\,\mathrm{F}(h,k,l)\,|\sum_{0}^{\mathrm{P}}\sum^{\mathrm{Q}}\sum^{\mathrm{R}}\cos\left[2\pi\left(\frac{t}{\tau}-\frac{x}{\lambda}+\phi\frac{(p,q,r)}{\lambda}\right)+\alpha\right]\\ &\quad -2\pi\mathrm{A}f_s\sum_{0}^{\mathrm{P}}\sum^{\mathrm{Q}}\sum^{\mathrm{R}}\left(\frac{h}{a}\Delta_a^{ps}+\frac{k}{b}\Delta_b^{qs}+\frac{l}{c}\Delta_c^{rs}\right)\\ &\quad\times\sin\left[2\pi\left(\frac{t}{c}-\frac{x}{\lambda}+\frac{\phi}{\lambda}\right)+\theta_s\right]\end{aligned} \tag{13}$$

where (P, Q, R) are the numbers of unit cells in each axial direction, and $\phi(p,q,r) = pa(\cos\alpha+\cos\alpha') + qb(\cos\beta+\cos\beta') + rc(\cos\gamma+\cos\gamma')$ (14) $(\alpha, \alpha';\ \beta, \beta';\ \gamma, \gamma')$ being the angles which the incident and diffracted

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[*] (h, k, l) are no longer necessarily integral.

directions make with the cell axes. (h, k, l) are now so chosen that the plane makes equal angles with these directions.

When the first summation is effected (13) becomes:—

$$\mathcal{A}_T = A \mid F(h,k,l) \mid \frac{\sin PL}{\sin L} \cdot \frac{\sin QM}{\sin M} \cdot \frac{\sin RN}{\sin N}$$

$$- 2\pi A f_s \sum_0^P \sum^Q \sum^R \left(\frac{h}{a} \Delta_a^{ps} + \frac{k}{b} \Delta_b^{qs} + \frac{l}{c} \Delta_c^{rs} \right)$$

$$\times \sin \left[2\pi \left(\frac{t}{\tau} - \frac{x}{\lambda} + \frac{\phi}{\lambda} \right) + \theta_s \right] \qquad (15)$$

where:—

$$\left. \begin{aligned} L &= \frac{\pi}{\lambda} a (\cos \alpha + \cos \alpha') \\ M &= \frac{\pi}{\lambda} b (\cos \beta + \cos \beta') \\ N &= \frac{\pi}{\lambda} c (\cos \gamma + \cos \gamma') \end{aligned} \right\} \qquad (16)$$

In the Laue-Bragg positions; $L = h\pi$, $M = k\pi$, $N = l\pi$ so that the first term is dominant. When these conditions are *not* satisfied, however, this term is of the order $A \mid F(h, k, l) \mid$.

Next, since there is *no* phase relationship between the Δ's in adjacent cells means displacements $\bar{\Delta}$ can be introduced giving:—

$$\sum_0^P \sum^Q \sum^R \left(\frac{h}{a} \Delta_a^{ps} + \frac{k}{b} \Delta_b^{qs} + \frac{l}{c} \Delta_c^{rs} \right) \sin \left[2\pi \frac{t}{\tau} - \frac{x}{\lambda} + \frac{\phi}{\lambda} \right) + \theta_s \right]$$

$$= \left(\frac{h}{a} \bar{\Delta}_a^s + \frac{k}{b} \Delta_b^s + \frac{l}{c} \bar{\Delta}_c^s \right) \sqrt{\sum_0^P \sum^Q \sum^R \sin^2 \left[2\pi \left(\frac{t}{\tau} - \frac{x}{\lambda} + \frac{\phi}{\lambda} \right) + \theta_s \right]} \qquad (17)$$

$$\bumpeq \left(\frac{h}{a} \Delta_a^s + \frac{k}{b} \bar{\Delta}_b^s + \frac{l}{c} \bar{\Delta}_c^s \right) \sqrt{\frac{PQR}{2}}, \qquad (18)$$

where the mean value of $\sin^2 x$ has been used.

This term is consequently much larger than the Laue-Bragg term at *non* lattice points and so *between* lattice points the intensity of X-ray diffraction is given by:—

$$I = 2\pi^2 f_s^2 \left(\frac{h}{a} \bar{\Delta}_a^s + \frac{k}{b} \bar{\Delta}_b^s + \frac{l}{c} \Delta_c^s \right)^2 P.Q.R.\ A^2 \qquad (19)$$

or, substituting for A and P.Q.R.

$$\frac{I}{I_0} = \frac{2\pi^2 e^4}{m^2 c^4} f_s^2 \frac{(1 + \cos^2 2\theta)}{2} \left(\frac{h}{a} \bar{\Delta}_b^s + \frac{k}{b} \bar{\Delta}_a^s + \frac{l}{c} \bar{\Delta}_c^s \right)^2 N\delta V, \qquad (20)$$

where N is the number of unit cells per unit volume and δV is the volume of the reflecting crystal.

This is to be compared with the value:—

$$\frac{I}{I_0} = \frac{e^4}{m^2c^4} \mid F \mid^2 \frac{1 + \cos^2 2\theta}{2} N^2 \, \delta V^2 \tag{21}$$

which obtains at the Laue-Bragg positions.

If there is more than one *independently* vibrating atom in the unit cell, (20) is replaced by:—

$$\frac{I}{I_0} = \frac{2\pi^2c^4}{m^2c^4} \frac{(1 + \cos^2 2\theta)}{2} \left[\sum_s f_s^2 \left(\frac{h}{a} \Delta_a^s + \frac{k}{b} \Delta_b^s + \frac{l}{c} \overline{\Delta}_c^s \right) \right] N\delta V \tag{22}$$

Should pairs of atoms be *associated* in vibration this formula is no longer valid and must be replaced by:—

$$\frac{I}{I_0} = \frac{2\pi^2e^4}{m^2c^4} \frac{(1 + \cos^2 2\theta)}{2} \left[2 \sum_{st} f_s^2 \left(\frac{h}{a} \Delta_a^s + \frac{k}{b} \Delta_b^s + \frac{l}{c} \Delta_c^s \right)^2 \right.$$

$$\left. \times \sin^2 \left(\frac{\theta_s - \theta_t}{2} \right) N\delta V \tag{23}$$

where the summation extends over all *pairs* of vibrating atoms.

Some deductions can be made from the foregoing equations. From (20) it is seen that the diffuse intensity will be greatest when (h, k, l) is *normal* to the direction of vibration and it will be zero for any plane parallel to this direction.

Again, from (22), if just two similar atoms are vibrating in different parts of the structure the diffuse scatter is greatest for planes normal to the line whose direction cosines are:—

$$(\lambda + \lambda'), \ (\mu + \mu'), \ (\nu + \nu')$$

where (λ, μ, ν), (λ', μ', ν') are the direction cosines of the vibration directions of the two atoms. Here again there is a zero of intensity, this time for planes parallel to the plane containing the two vibration directions.

In the case of more than two independently vibrating atoms there will be, in general, no zero and the iso-intensity surfaces will be ellipsoids.

Using (23), and considering only one *pair* of vibrating atoms it is seen that the state of affairs is much more complex. For planes normal to the vibration direction the intensity is periodic and decays due to the variation in the atomic scattering factor f.

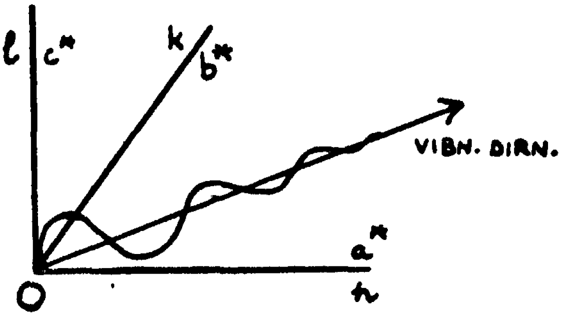

FIG. 1

When symmetry of the space group is added the variation is even more involved but in general the symmetry of the pattern follows that of the lattice.

5. CONCLUSION

The preceding treatment is to some extent naïve but has the virtue of extreme simplicity. When compared with the results of experiment, the agreement is quite good from the qualitative point of view. It is not worth attempting the evaluation of, for example, the summations for the σ_s and σ_c of (6) or the integrals of (8) until more is known regarding the detailed causes of lattice perturbation. When this knowledge is available there are several methods of handling summations of the types considered which can be applied to specific cases.

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RECHERCHES SUR LES CRISTAUX DANS LE SPECTRE INFRAROUGE

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LE Laboratoire des Recherches physiques à la Sorbonne ne s'est pas spécialisé dans l'étude des spectres infrarouges des cristaux, ayant surtout consacré une partie de son activité à la mesure de l'absorption et de la réflexion, dans l'infrarouge, par des composés organiques ou minéraux, ainsi qu'à la détermination consécutive des structures moléculaires. Néanmoins, nous avons eu l'occasion de diriger plusieurs recherches concernant le comportement des cristaux dans l'infrarouge, et aussi d'y participer personnellement. Par suite, nous semble-t-il intéressant de donner ici une synthèse rapide des résultats obtenus.

Nous passerons successivement en revue:

I.—L'absorption des cristaux dans le proche infrarouge (en lumière naturelle ou polarisée,;

II.—Les spectres infrarouges des poudres cristallines;

III.—La détermination des indices de réfraction des cristaux par une méthode interférentielle (infrarouge moyen);

IV.—La pyroélectricité des cristaux et son application à la détection des radiations infrarouges.

* * * *

I.—L'absorption des cristaux dans le proche infrarouge (en lumière naturelle ou polarisée).—On peut examiner les cristaux, dans l'infrarouge, soit par réflexion, soit par transmission. La première méthode a donné lieu, on le sait, à la célèbre méthode des rayons restants. Mais il existe souvent, pour un cristal, des domaines étendus, dans lesquels les pouvoirs réflecteurs restent faibles, et même, pour certains minéraux, les variations de ces pouvoirs réflecteurs, dans tout le spectre, demeurent fort réduites. C'est ce qui a conduit à passer à l'examen par transmission. Jusqu'ici, au Laboratoire des Recherches physiques, à la Sorbonne, on n'a étudié les lames cristallines, d'une manière systématique, que dans le proche infrarouge. Nous rappellerons que, dans cette région, les recherches restent relativement peu nombreuses. Parmi elles, celles de Coblentz[1] représentent vraiment le travail le plus complet, quoique un peu ancien. Dans les recherches plus récentes se placent celles de Lyon et Kinsey[2], Passerini,[3] Matossi et Bronder,[4] Plyler,[5] van Arkel et Fritzius,[6] Ellis[7] &.... Mais la technique prend surtout son intérêt, lorsque l'on recourt à des radiations polarisées. Parmi les travaux, dont certains remontent déjà à la fin du siècle dernier, nous citerons ceux de Koenigsberger[8] Merrit,[8] Carvallo,[9] Goens,[10] Reinkober,[11] et, dans de plus récents, ceux de Ellis et Bath,[12] Valasek[13] &....

Dans l'ensemble, il existe relativement peu de recherches sur le spectre d'absorption des cristaux dans le proche infrarouge.

Mlle J. Louisfert, en utilisant un spectrographe à prisme de verre (flint extra-dense) et, comme polariseur un prisme de Foucault, a mesuré, entre 0,8 et 2,5 μ, l'absorption de 12 cristaux hydratés: une série de silicates, dont 4 zéolites (analcime, mésotype, heulandite, apophyllite), la topaze, la muscovite, le béryl, une série de sulfates (gypse, SO_4Cd,8/3 H_2O, SO_4Zn, 7 H_2O, SO_4Cu,5 H_2O).[14] Avec chacun d'eux, on a déterminé des courbes de transmission, pour des orientation bien définies du plan de polarisation par rapport aux axes cristallographiques. Il apparaît, dans chaque cas, une dizaine de bandes d'absorption, dont quelques unes se présentent comme très fortes. *Les variations en position de ces maxima, avec la rotation du plan de polarisation des radiations incidentes, restent généralement peu importantes, alors que l'intensité des bandes d'absorption varie souvent beaucoup, au point même d'arriver à la disparition de certaines d'entre elles.* (Dans les Fig. 1 et 2, chaque courbe correspond à une position différente du polariseur.

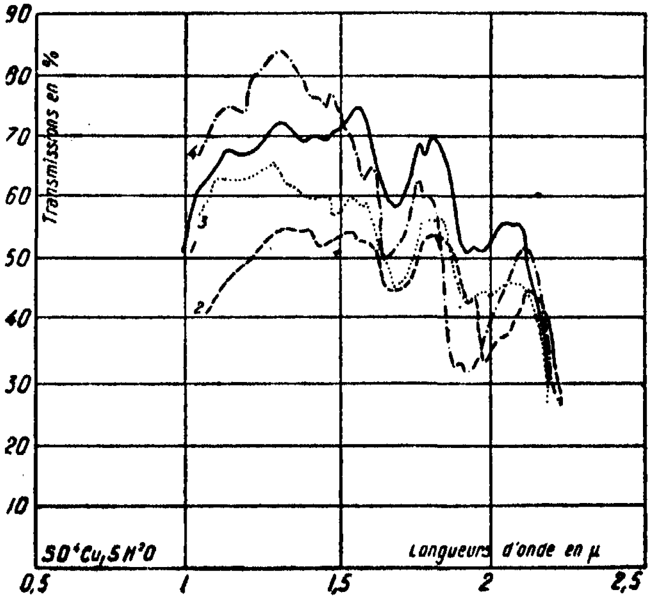

Fig. 1

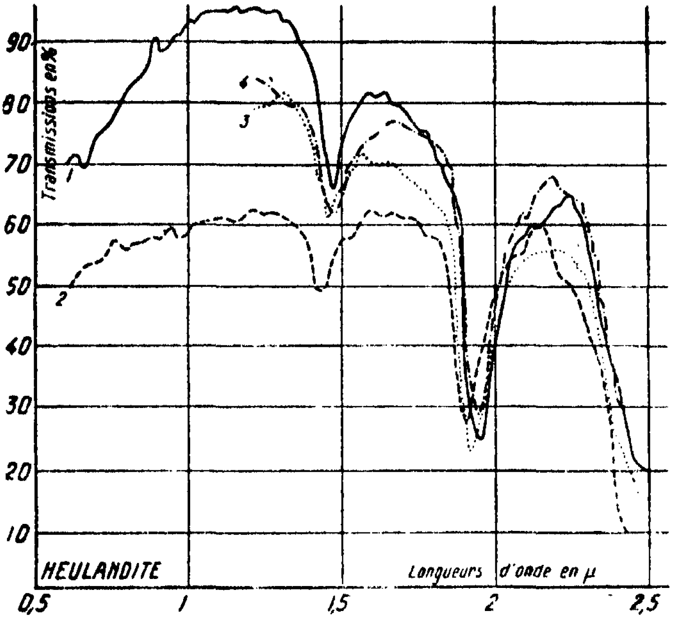

FIG. 2

Ce travail a eu pour objet: 1°) en étudiant la position des bandes d'absorption, d'un cristal à un autre, de préciser la maière dont l'eau se trouve liée dans ces minéraux, et 2°) d'essayer d'utiliser les variations en intensité des bandes pour orienter les molécules dans l'édifice cristallin. Nous développerons un peu ces deux points de vue.

La plupart des bandes d'absorption qui, ont été mesurées par Mlle J. Louisfert dans le proche infrarouge, proviennent de la présence de l'eau dans les cristaux. D'après les études d'autres auteurs, on sait que les maxima d'absorption de l'eau liquide, dans cette région, se déplacent vers de plus courtes longuers d'onde, quand l'eau prend l'état de vapeur. D'une manière plus précise, les vibrations de valence symétrique et antisymétrique de la molécule H O H, considérée comme angulaire (Fig. 3), pour l'état liquide, se placent à 2,90 μ (ν_1) et 2,79 μ (ν_3), et, pour l'état de vapeur,

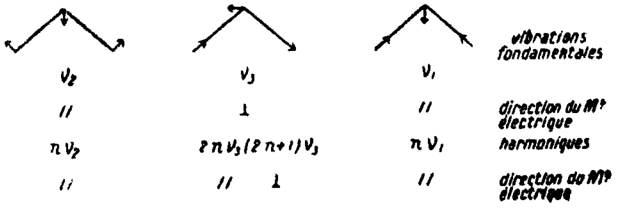

FIG. 3

à 2,76 μ (ν_1) et 2,66 μ (ν_3). De cette manière, dans le changement d'état, se déplacent de 1,55 à 1,38 μ, d'une part, et de 1,95 à 1,87 μ, d'autre part, des bandes particulièrement importantes du proche infrarouge, qui correspondent respectivement aux vibrations: 2 ν_1 ou 2 ν_3 ou $\nu_1 + \nu_3$, et $\nu_1 + \nu_2$ ou $\nu_2 + \nu_3$. Dans les cristaux, les maxima d'absorption mesurés se placent entre les nombres extrêmes, correspondant à l'eau liquide et à l'eau à l'état de vapeur, ce qui permet, inversement, de connaître la manière dont l'eau est liée dans la molécule, en accord avec des recherches antérieures, par exemple, celles d'Ellis et de ses collaborateurs. La même conclusion s'applique aux vibrations des groupements OH, contenus dans les molécules, avec la différence qu'il n'existe, dans ces conditions, qu'une vibration fondamentale caractéristique, avec ses harmoniques successifs.

Ainsi, les liaisons OH avec le reste de la molécule sont peu prononcées pour la topaze et la muscovite (maximum à 1,40 μ). L'eau se présente comme sensiblement libre dans le béryl (maximum à 1,40 μ), un peu plus liée dans l'analcime (maximum à 1,42 μ) et le mésotype (maximum à 1,43 μ), la heulandite (maximum à 1,45 μ), très liée, par contre, dans les sulfates de cadmium et de zinc (maximum à 1,48 μ). Pour le sulfate de cuivre, à 5 molécules d'eau, les deux maxima à 1,37 et 1,46 μ indiquent la présence de deux espèces d'eau, conformément aux conclusions bien connues des chimistes. Le cas du gypse présente une complication plus grande en raison du nombre plus important des bandes observées.

Dans la fig. 3, sont représentés les trois modes de vibration d'une molécule triatomique angulaire comme H_2O. Le moment électrique vibre parallèlement à l'axe binaire dans les vibrations symétriques ν_1 et ν_2, et perpendiculairement pour la vibration antisymétrique ν_3. En ce qui concerne tous les harmoniques, pairs ou impairs des vibrations ν_1 et ν_2, le moment électrique continue à vibrer parallèlement à l'axe binaire de la molécule; mais, pour la vibration ν_3, les harmoniques pairs possèdent un moment électrique parallèle à l'axe, et les harmoniques impairs un moment électrique perpendiculaire à l'axe. L'intensité d'une bande d'absorption infrarouge est liée, on le sait, à la variation du moment électrique: si celle-ci reste nulle, la vibration correspondente est inactive dans l'absorption. En particulier, si, dans la vibration considérée, le moment électrique ne possède pas de composante perpendiculaire au plan de polarisation de la lumière, la bande correspondante manquera dans le spectre. Au contraire, elle prendra une intensité maximum, si le moment électrique est lui-même perpendiculaire au plan de polarisation.

Mlle J. Louisfert a utilisé ces remarques pour essayer d'orienter les molécules d'eau dans les cristaux, au moyen des variations qu'elle a observées dans les spectres d'absorption. On sait que les rayons X ne donnent pas facilement l'emplacement des atomes d'hydrogène, et l'infrarouge prend ainsi une grande importance pour contribuer à l'étude de la structure cristalline. La difficulté réside en ce que les vibrations de valence ν_1 et ν_3, étant fort voisines, il est souvent difficile de savoir, dans l'attribution des modes de vibration aux bandes observées, s'ils 'agit de 2 ν_1 ou de 2 ν_3, ou encore de $\nu_1 + \nu_3$. Néanmoins, cette méthode a donné d'intéressants résultats, en particulier pour le gypse, la heulandite &....

Yeou Ta a repris, sur un cristal d'iodoforme (CHI_3),[15] les expériences d'Ellis et Bath[12] sur le pléochroisme des cristaux dans l'infrarouge, avec l'application aux modes de vibration de la liaison carbone-hydrogène. Opérant d'abord en lumière naturelle, il a montré que la bande d'absorption à 17·175 Å n'apparaissait pas lorsque la lamelle se trouvait placée perpendiculairement au faisceau incident, et qu'elle réapparaissait en inclinant légèrement le cristal. Par contre, les bandes à 14·610, 19·705, et 24·780 Å ne présentaient pas de changement notable dans les mêmes expériences. On admet que la bande à 17·175 Å correspond au premier harmonique de la vibration C–H. Ce qui précède montre qu'elle s'effectue dans la direction de la liaison C–H, et que celle-ci est bien orientée suivant l'axe du cristal. En effet, seulement lorsque la lamelle se trouve inclinée par rapport au faisceau, le vecteur électrique possède une composante parallèle à l'axe du cristal, condition nécessaire à l'apparition de la bande due à la vibration C–H. Des expériences en lumière polarisée, avec des lamelles inclinées sur le faisceau, confirment ces résultats.

Ces conclusons analogues ont été obtenues par le même auteur[16] avec la brucite, $Mg(OH)_2$, en étudiant une bande vers 1,4 μ, qui correspond au premier harmonique de la vibration O–H. Cette liaison doit être parallèle à l'axe sénaire du cristal, qui se présente comme perpendiculaire au plan de clivage, car, comme précédemment avec le cristal d'iodoforme, la bande disparaît lorsque la lame reçoit le faisceau sous l'incidence normale. En collaboration avec Cl. Duval et R. Freymann,[17] nous avons confirmé ces résultats en les étendant à la vibration de déformation du groupement OH. Sous l'incidence normale, une lamelle relativement épaisse de brucite (0,7 mm.) ne présentait aucun maximum d'absorption, alors qu'une mince couche (inférieure à 0,01 mm.) d'oxyde de magnésium hydraté ou de brucite en poudre donnait lieu à de forts maxima respectivement vers 1467 et 1487 cm.$^{-1}$ Dans cette dernière expérience, la poudre présente des axes moléculaires orientés au hasard par rapport à la direction du faisceau incident, de sorte que la variation du moment électrique, au cours de la vibration OH, devient statistiquement différente de zéro: ce qui conduit à une absorption sélective.

II. Les spectres infrarouges des poudres cristallines.—Depuis 1938, nous avons développé, d'une manière systématique, au Laboratoire des Recherches physiques à la Sorbonne, les études sur les composés organiques ou minéraux à l'état pulvérulent. La méthode apparaît comme absolument générale, car plus de mille substances, appartenant à des types moléculaires les plus divers, ont été ainsi examinées. On obtient, avec une mince couche de poudre finement broyée, un spectre aussi net que s'il s'agissait de substances liquides ou gazeuses, ou de lamelles solides. Il faut seulement que la longueur d'onde des radiations utilisées se présente comme suffisamment grande pour que la diffusion ne joue qu'un rôle restreint. Avec de nombreux collaborateurs, nous avons exploré le domaine de 6 à 20 ν, et M. Parodi[18] a montré que la méthode donnait d'excellents résultats vers de plus grandes longueurs d'onde (80 μ environ). Avec cette technique, tout en ne disposant que d'une quantité de matière très réduite, on peut étudier une foule de substances, dont l'examen aurait été pratiquement impossible, en raison de leur insolubilité dans tous les solvants utilisables, de leur décomposition au cours de la fusion, ou bien de l'existence de points de fusion élevés. De plus, on est certain d'étudier les composés dans l'état exact où ils se trouvent, sans avoir à craindre une modification. Cette circonstance se montre particulièrement précieuse pour l'étude de substances possédant plusieurs degrés d'hydratation.

Avec divers collaborateurs, nous avons transposé cette technique au cas des cristaux, mais les résultats n'ont pas encore été publiés. Lorsque l'on étudie la transmission d'une poudre cristalline, on peut supposer qu'une bonne partie des vibrations du réseau n'apparaîtra pas dans les spectres, en particulier par suite de l'arrangement incohérent des particules. Mais on peut obtenir, exactement comme nous l'avons vu pour la brucite, des renseignements sur la nature des groupements chimiques contenus dans les molécules examinées. Comme l'on pouvait s'y attendre, le gypse et l'anhydrite en poudre reproduisent les maxima d'absorption caractéristiques de SO_4. Mais, si nous examinons des ortho-silicates tels que la willemite (SiO_4Zn_2), le zircon (SiO_4Zr) ou l'orangite (SiO_4Th), et la forsterite (SiO_4Mg_2), la structure d'une région d'opacité vers 11 μ, attribuable à la présence de SiO_4 se présente comme différente. Avec le premier minéral, on note trois maxima distincts (10,31 10,94 et 11,56 μ), dont le deuxième est beaucoup plus intense que les autres, alors que les trois silicates restants ne donnent qu'une bande large, plus ou moins déplacée. Avec la phénacite (SiO_4Gl_2), on retrouve bien trois maxima, comme dans la willemite, mais considérablement déplacés vers de plus courtes longueurs d'onde (9,63 10,09 10,62 μ). L'interprétation est à chercher dans une structure différente du groupement SiO_4. S'il possède une structure tétraédrique régulière, il ne doit donner naissance, dans cette région qu'à une seule bande forte et étroite. Mais s'il se trouve déformé, dans le cristal, par les molécules avcisinantes, ou par des liaisons dont ne fait pas mention la formule chimique, la vibration triplement dégénérée se décompose en deux ou trois bandes distinctes, ou bien l'absorption s'étend sur un large domaine En collaboration avec Cl. Duval, nous avons étudié une cinquantaine d'orthophosphates et nous avons montré que, suivant l'aspect du spectre, on pouvait en déduire la symétrie du groupement PO_4 dans les composés étudiés. Avec la vivianite (PO_4Fe_3, 8 H_2O) ou l'autunite $(PO_4)_2$ $(UO_2)_2Ca$, 8 H_2O, le spectre comprend, entre 6 et 15 μ, beaucoup plus de bandes que n'en comporte une symétrie tétraédrale pour le groupement PO_4.

Ces quelques exemplees montrent que, *lorsque l'on ne possède pas une lamelle de dimensions suffisantes pour obtenir un spectre d'absorption infrarouge, la méthode des poudres permet néanmoins de caractériser les groupements contenus dans les molécules considérées comme isolées.*

III. La détermination des indices de réfraction des cristaux par une méthode interférentielle (*infrarouge moyen*).—Il est très important, pour mettre au point les propriétés des cristaux dans l'infrarouge, de connaître leur dispersion dans ce domaine. Malheureusement, dès que l'on dépasse des longueurs d'onde de quelques μ, l'absorption devient si grande qu'il n'est plus possible de recourir à la méthode classique du prisme. D'ailleurs, celle-ci nécessiterait des échantillons de taille très supérieure à ceux que l'on peut se procurer. Aussi, Mme J. Ramadier-Delbès a-t-elle abordé ce problème par une méthode interférentielle.[19]

On commence par tailler une lamelle cristalline très mince (quelques centièmes de mm.), ayant, par exemple, 5 mm. de coté. Cette opération présente des difficultés, qui sont accrues par la nécessité d'orienter convenablement la lamelle par rapport aux axes cristallographiques. On produit un dépot métallique, opaque sur l'une des faces et semi-transparent sur l'autre. On enregistre, au moyen d'un spectrographe à miroirs et à prisme de sel gemme, avec une pile thermoélectrique comme détecteur, les franges d'interférences produites entre les radiations réfléchies par la surface supérieure du cristal (semi-métallisée), et celles qui sont renvoyées par la métallisation opaque de la surface inférieure, après avoir traversé deux fois l'épaisseur *e* du cristal (Fig. 4).

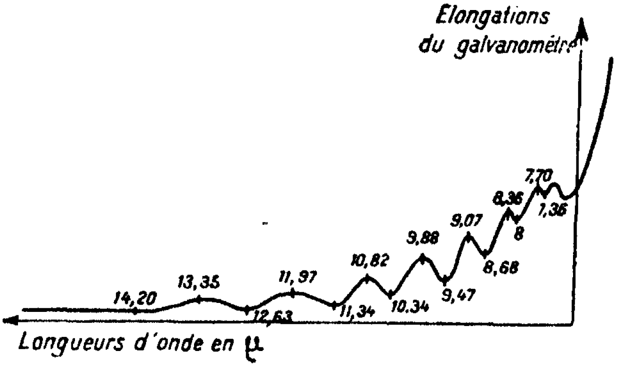

FIG. 4. Interférences d'une lame mince de flnorine $z = 2\,e\ \cos\, r = 68,6\,\mu$.

Si l'on désigne par n l'indice de réfraction du cristal pour la longueur d'onde λ, r l'angle de réfraction, les minima d'interférences apparaîtront aux positions données par la relation:

$$2\,n\,e \cos.\, \mathrm{r} = k\lambda.$$

On détermine $Z = 2\,e\ \cos.\ r$ par des mesures effectuées dans le visible, en comptant le nombre des cannelures noires entre deux longueurs d'onde connues, ce qui permet de calculer n, si l'on connait k, ordre d'interférence. D'une frange à la suivante, dans le visible comme dans l'infrarouge, k varie bien d'un nombre entier; mais il ne représente pas nécessairement un nombre entier, en raison du changement de phase, produit par la réflexion sur la surface métallisée de la lamelle.

Mme J. Ramadier-Delbès est en train d'appliquer avec succès cette méthode à la fluorine, où elle a pu prolonger au delà de $14\,\mu$ la connaissance des indices qui s'arrêtait vers $9\,\mu$. Pour la calcite, entre 8 et $14\,\mu$, l'indice de réfraction varie entre 6 et 2. D'autres cristaux sont à l'étude, et donneront certainement des résultats intéressants, puisque la dispersion anomale représente un phénoméne relativement rare dans le spectre visible, mais très fréquent dans le spectre infrarouge.

Cette méthode avait déjà été ' appliquée à la calcite par Taylor et Rideal[20]; mais avec une précision bien moindre, qui tenait à ce que ces auteurs observaient des franges par transmission, avec des lamelles non métallisées, et surtout parcequ'ils éliminaient l'ordre d'interférence entre deux équations du type précédemment indiqué, donnant la position des franges noires, en supposant l'indice de réfraction du cristal constant dans l'intervalle de longueur d'onde considéré.

IV. La pyroélectricité des cristaux et son application à la détection des radiations infrarouges.—Lorsque l'on fait tomber, sur un cristal pyroélectrique, des radiations qui sont absorbées par lui, il s'échauffe et se polarise suivant son axe électrique. YeouTa[21] a taillé des lamelles de tourmaline en forme de lames à faces parallèles, perpendiculaires à l'axe, rectangulaires ou en forme de disque. Les radiations arrivent ainsi que l'indique la Fig. 5, et les faces terminales sont recouvertes d'un dep^{O}t métallique servant d'électrode. L'effet pyroélectrique reste toujours très petit, mais,si l'on décelait une charge de 10^{-15} coulombs/cm^2, on pourrait mesurer une variation de température du cristal d'un millionième de degré centigrade. L'auteur s'est assuré que l'effet produit par l'éclairement est essentiellement dû à l'infrarouge. Comme, d'autre part, une partie au moins de l'effet est modulable, il en résulte que le cristal pyroélectrique peut servir de détecteur dans la partie infrarouge du spectre (la limite d'utilisation n'étant pas encore précisée). Il serait possible de perfectionner la méthode, en prenant un cristal possédant une constante pyroélectrique plus élevée que la tourmaline, et une constante diélectrique plus petite: en fait, Yeou Ta a trouvé que l'acide tartrique droit se montrait quatre ou cinq fois plus sensible que la tourmaline.

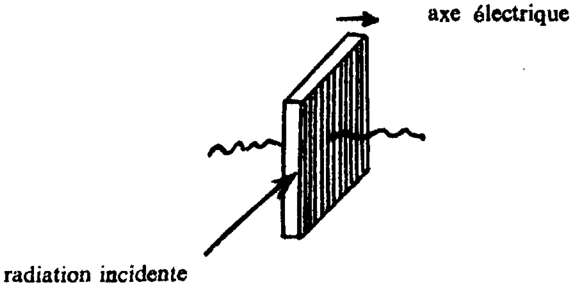

FIG. 5

* * * *

Ce qui précède montre que l'étude des cristaux, dans le spectre infrarouge, si elle n'a pas constitué un des objectifs principaux au Laboratoire des Recherches physiques à la Sorbonne, a néanmoins conduit à des résultats intéressants. Il nous est malheureusement impossible, dans le cadre de cet article, de résumer un important travail, éxécuté sous notre direction par M. Parodi:[18] Recherches dans l'infrarouge lointain par la méthode des rayons restants. On trouvera dans cette thèse un ensemble de résultats théoriques et expérimentaux, qui intéresse directement les cristaux, et qu'il est nécessaire de consulter dans le texte original.

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LES OSCILLATIONS EXTERNES DU RESEAU CRISTALLIN DE LA CALCITE

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Summary.—The normal modes of vibration of the unit cell of crystals built up by complex units (molecules or complex ions) may be classified into internal modes of vibration of these units and into external or lattice oscillations where these units move like rigid bodies towards the lattice. These external vibrations are generally subdivided into translatory modes and rotatory modes of oscillation. This subdivision is not a rigorous one: the translatory motions and the rotatory motions are ideal forms of motion, but the real oscillations of the lattice must be considered as couplings of these two ideal modes. These couplings, determined by the symmetry of the lattice forces, are only possible between motions of the unit cell belonging to the same class of symmetry. The example of calcite is considered to illustrate these coupling effects and to count the number of different low frequency oscillations active in the Raman Spectrum of the crystal and in its infrared absorption spectrum.

Le spectre Raman d'un cristal de calcite CO_3Ca, a été étudié par plusieurs auteurs qui ont déterminé les caractères de polarisation des différentes raies en fonction de l'orientation du cristal et de l'état de polarisation de la lumière incidente.[1] Des mono-cristaux de nitrate de sodium NO_3Na qui ont la même structure cristalline que la calcite, ont été également étudiés et ont donné des résultats analogues en ce qui concerne le nombre, la fréquence et la polarisation des raies.[2] En dehors des raies qui sont dues aux vibrations internes de l'ion complexe CO_3 (ou NO_3) et qu'on retrouve, avec des fréquences peu différentes, dans tous les carbonates ou nitrates à l'état solide, fondu ou dissous, les cristaux de calcite et de nitrate de sodium présentent chacun deux raies Raman de faible fréquence (156 cm.$^{-1}$ et 283 cm.$^{-1}$ pour la calcite, 100 cm.$^{-1}$ et 189 cm.$^{-1}$ pour le nitrate de sodium). Ces raies de faible fréquence sont caractéristiques du réseau cristallin et disparaissent lorsque l'arrangement du réseau est détruit par fusion ou dissolution du cristal. Elles sont très sensibles à une variation de température: un échauffement du cristal les rend plus diffuses et les rapproche de la raie excitatrice.[3] Leurs fréquences sont du même ordre de grandeur que les fréquences d'absorption de ces cristaux observés dans l'infrarouge lointain[4] et qu'on attribue à des vibrations de translation des cations par rapport aux anions.

Dans une note parue en 1939, C. V. Raman et T. M. K. Nedungadi[5] ont montré que la polarisation caractéristique des deux raies Raman de basse fréquence du nitrate de sodium suggère leur attribution à des mouvements de pivotement (oscillations de rotation) des anions NO_3 dans le réseau. A cause de la forte anisotropie optique de ces ions leurs changements d'orientation dans le réseau doivent en effet se manifester fortement dans le spectre de diffusion.

A. Kastler et A. Rousset[6] ont montré que les deux raies Raman de basse fréquence de la calcite ont la même origine.

Mais par suite de la symétrie ternaire des anions complexes et de leur entourage cristallin, les mouvements de pivotement de ces anions, autour d'un axe de leur plan doivent être dégénérés et la théorie ne prévoyait qu'une seule fréquence de pivotement, alors que l'expérience fournit deux raies Raman ayant les caractères de raies de pivotement. Dans une note récente deux auteurs italiens L. Giulotto et G. Olivelli[7] ont donné la clef du mystère: ils ont montré que la disposition des ions dans le réseau et la symétrie des forces qui s'exercent entre proches voisins entraînent un couplage entre oscillations de translation et oscillations de rotation, et que ce couplage est responsable de l'apparition de deux raies Raman. L'auteur du présent article a montré[8] que les modes de mouvement désignés par ‘ oscillations de translation ’ et ‘ oscillations de rotation ’ ne sont en général que des types idéaux, et que les oscillations fondamentales réelles sont presque toujours des superpositions de ces deux types, oscillations au cours desquelles chaque centre matériel décrit une trajectoire qui est en général de forme hélicoïdale. Il se propose ici d'illustrer ce fait par l'exemple de la calcite en envisageant les diverses oscillations externes de ce type de réseau.

La maille élémentaire de la calcite contient deux anions complexes CO_3 et deux cations Ca, alignés le long de l'axe optique du cristal (Fig. 1). Le long de cet axe les cations alternent régulièrement avec les anions. Ces derniers sont plans et ont la symétrie d'un triangle équilatéral qui est perpendiculaire à l'axe optique du cristal. Les deux anions de la maille élémentaire ont leurs sommets opposés (staggered configuration). Chaque maille élémentaire contient donc quatre éléments constitutifs distincts (deux anions CO_3 que nous distinguerons par les lettres A et B et deux cathions Ca que

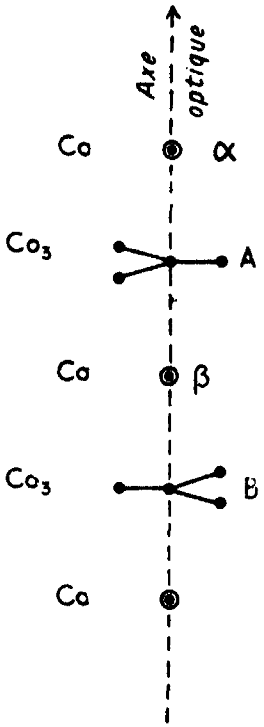

FIG. 1

nous distinguerons par les lettres α et β). Chacun de ces éléments constitutifs forme, par sa répétition dans chaque maille un réseau simple d'éléments congruents. L'examen d'un modèle cristallin montre que ces éléments constitutifs sont disposés en couches perpendiculaires à l'axe optique du cristal. La Fig. 2 donne une coupe d'ensemble du réseau par un plan de symétrie normal à un axe binaire du réseau (plan de section principale d'un spath calcaire). Les petits cercles représentent des cations Ca situés dans le plan de coupe; les petites croix correspondent chacune à deux cations, l'un en avant, l'autre en arrière du plan de coupe, et formant avec les cations voisins situés dans le plan de coupe un pavage de triangles équilatéraux dans un plan perpendiculaire à l'axe optique du cristal. Les deux orientations opposées des anions CO_3 sont indiquées sur la figure (en réalité, les axes binaires de ces anions ne sont pas dans le plan de coupe, mais à 30° de celui-ci). La coupe fait voir la disposition des éléments congruents en couches successives A, α, B, β, etc..... Chaque anion a comme plus proches voisins six cations Ca, dont trois sont disposés en un triangle équilatéral au dessus de l'anion, les trois autres en un triangle équilatéral, d'orientation

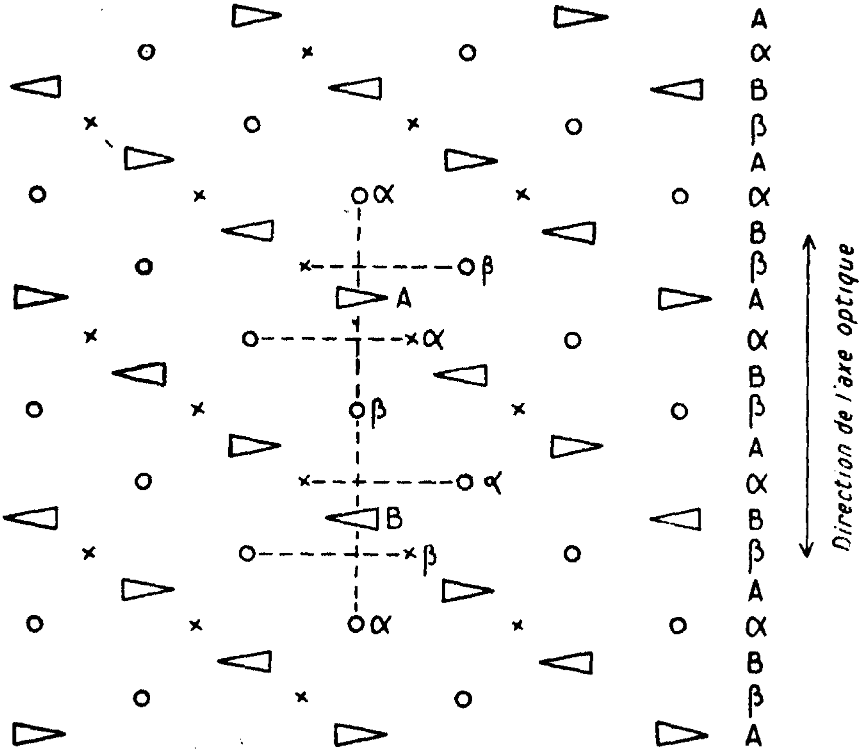

Fig. 2

opposée au-dessous de l'anion. L'orientation de ces triangles est la même autour des anions de type A et des anions de type B, mais la parité des couches est différente. Un anion A a au-dessus de lui un triangle de Ca β, au-dessous de lui un triangle de Ca α. L'inverse a lieu pour un anion B.

A l'état d'équilibre chaque atome d'oxygène d'un anion CO_3 se trouve à égale distance de ceux cathions Ca, appartenant aux couches voisines de part et d'autre. Il est naturel d'admettre, avec les auteurs italiens, que des forces s'exercent entre les cathions et les atomes d'oxygene des anions. Nous ignorons le sens de ces forces, nous admettrons, pour fixer les idées, qu'elles sont attractives. A l'état d'équilibre ces forces se compensent. Elles interviennent lorsque les ions se déplacent, et nous allons voir qu'elles entrainent une interdépendance entre les oscillations de translation et les oscillations de rotation des ions.

Jean Cabannes[9] a dénombré et classé les divers types d'oscillations fondamentales de la maille de calcite: Suivant leurs caractères de symétrie ces oscillations peuvent se classer en oscillations symétriques par rapport à l'axe ternaire (symbole A) et oscillations dégénérées par rapport à cet axe (symbole E). Chaque cation Ca est un centre de symétrie du réseau indéfini, et les oscillations peuvent aussi se classer en oscillations symétriques par rapport à ce centre (suffixe *g*) ou antisymétrique par rapport à lui (suffixe *u*). Enfin, il est commode (mais comme nous verrons non essentiel de distinguer des mouvements de translation et des mouvements de pivotement. On peut ainsi distinguer dix types de mouvement qui se classent en cinq classes de symétrie distinctes A_{2g}, E_g, A_{1u}, A_{2u}, E_u. La Fig. 3 montre ces formes de mouvements des éléments de la maille. Remarquons que les deux mouvements de translation E_u(1) (translation mutuelle des cations et des anions) et E_u(2) (translation mutuelle des cathions α et des cations β) appartiennent à la même classe de symétrie et que le chiffre ajouté entre parenthèse a uniquement pour but de les distinguer. Rappelons que les mouvements symétriques par rapport au centre (*g*) sont toujours inactifs en absorption infrarouge alors que les mouvements antisymétriques par rapport à ce centre (*u*) ne peuvent pas apparaître en effet Raman. Les oscillations de translation A_{2u} et E_u(1) sont actives en infrarouge, le moment électrique de la première étant parallèle à l'axe, le moment électrique de la seconde perpendiculaire à l'axe. Les oscillations de translation A_{1u} et E_u(2) ainsi que les oscillations antisymétriques de pivotement ne produisent pas de moment électrique et ne se manifestent pas dans le spectre infrarouge.

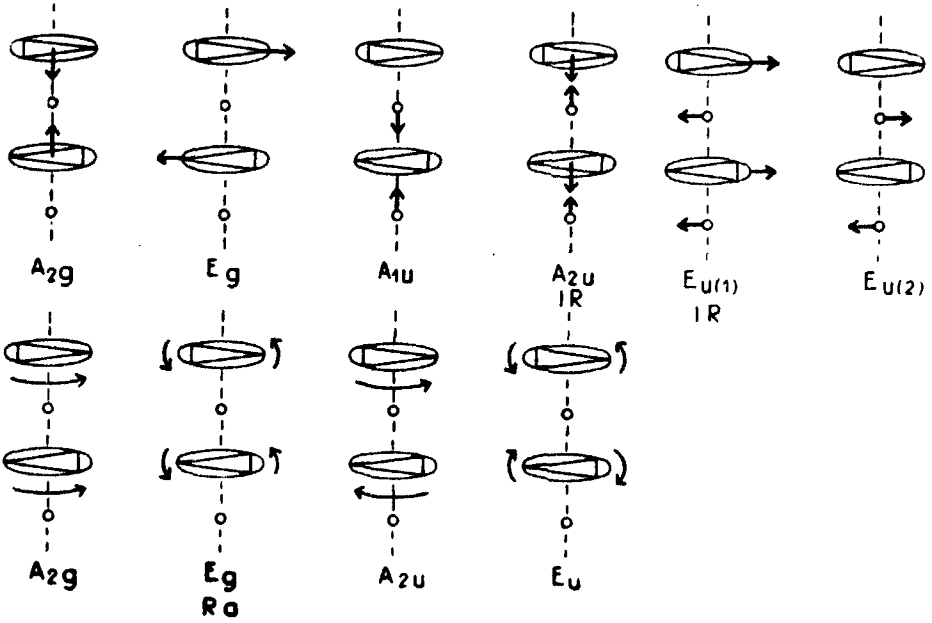

Fig. 3

Le mouvement de pivotement E_g doit apparaître fortement dans la diffusion; l'oscillation de torsion A_{2g} des ions CO_3 autour de l'axe ternaire ne peut se manifester que faiblement dans l'effet Raman, et à la condition d'admettre que le mouvement de torsion déforme l'ellipsoide de polarisabilité des ions CO_3 ce qui n'est pas impossible. Mais la déformation ne peut être que du second ordre et ne peut pas se manifester sur la fréquence fondamentale. Des considérations de symétrie montrent que les mouvements de translation A_{2g} et E_g ne peuvent pas se manifester en diffusion sur la fréquence fondamentale. Les figures 4 à 9 illustrent les effets de couplage entre les mouvements de translation et de rotation de même classe de symétrie. Chaque figure représente au milieu un ion CO_3 (à gauche l'ion A, à droite l'ion B) et autour de lui les six ions Ca qui sont ses plus proches voisins, l'ensemble étant projeté sur un plan perpendiculaire à l'axe optique. Les cercles noirs (signe +) représentent des ions Ca au-dessus de l'ion CO_3, les cercles clairs (signe —) des ions Ca au-dessous de l'ion CO_3.

La Fig. 4 montre que la torsion A_{2g} des ions CO_3 autour de l'axe ternaire entraîne une translation A_{2g} de ces ions parallèlement à l'axe optique. En effet, la rotation de l'ion CO_3 de type A éloigne les atomes d'oxygène de cet ion des ions Ca au-dessus et le rapproche des ions Ca au-dessous dont l'attraction l'emporte (signes —). En tournant dans le sens des aiguilles de la montre, l'ion CO_3 de type A se trouve donc poussé vers le bas, alors que l'ion CO_3 de type B (figure de droite) se trouve sollicité vers le haut. La rotation A_{2g} et la translation A_{2g} se couplent donc et leur couplage engendre deux oscillations réelles de forme hélicoïdale et de fréquences distinctes. Ces oscillations sont inactives en absorption infrarouge et en diffusion.

La Fig. 5 montre que la translation E_g de l'ion CO_3 perpendiculairement à l'axe optique entraîne un pivotement de cet ion autour de l'axe de translation par suite de la dissymétrie des forces attractives produite par la translation. Mais les mouvements de translation et de pivotement qui se couplent ainsi sont tous les deux de la classe E_g et ne se manifestent pas en absorption infrarouge. Ce couplage explique l'apparition des deux raies Raman de faible fréquence, et l'intensité relative de ces deux raies permet d'evaluer la part que prend le pivotement à chacune de ces deux oscillations.

La Fig. 6 illustre le couplage entre l'oscillation de torsion A_{2u} et l'oscillation de translation parallèle à l'axe optique de même classe de symétrie. La torsion des deux ions CO_3 de la maille, en sens inverse, entraîne, en effet, des forces d'attraction qui s'exercent sur les deux ions CO_3 dans le même sens (vers le bas dans le cas de la figure). Ce couplage crée deux fréquences d'absorption infrarouges, le vecteur électrique absorbé étant parallèle à l'axe

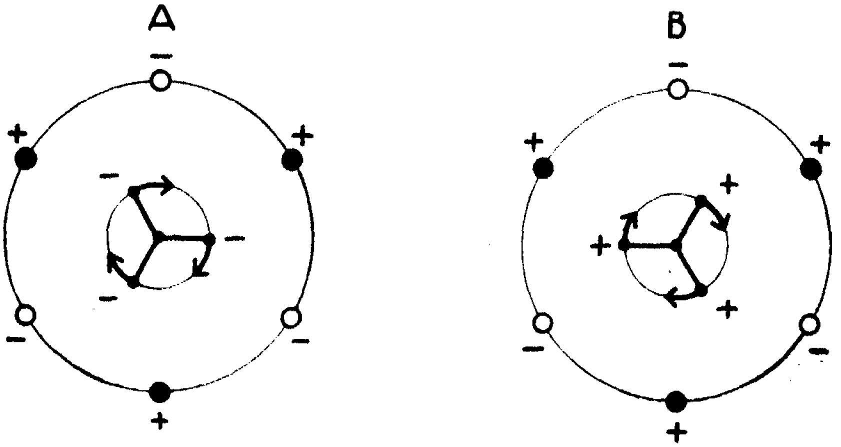

Fig. 4

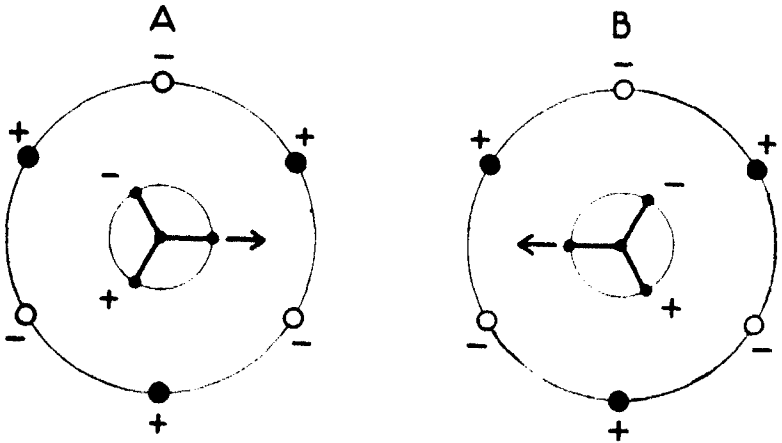

Fig. 5

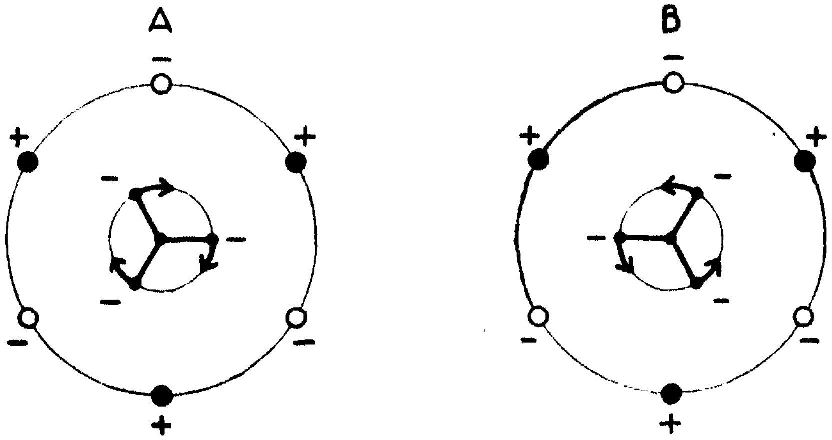

Fig. 6

optique (106 cm.$^{-1}$ et 357 cm.$^{-1}$ pour CO_3Ca, 71 cm.$^{-1}$ et 217 cm.$^{-1}$ pour NO_3Na).

La Fig. 7 montre que l'oscillation de translation E_u (1), perpendiculaire à l'axe, entraîne un pivotement antisymétrique des deux ions CO_3 autour de leurs axes de translation.

La Fig. 8 montre que l'oscillation mutuelle des deux réseaux partiels Ca (α) et Ca (β) se couple avec ce même pivotement; et la Fig. 9 illustre l'effet inverse: le pivotement antisymétrique des deux ions CO_3 A et B de la maille écarte l'ion Ca, qui se trouve entre eux, de l'axe ternaire. Dans l'hypothèse de forces attractives cet ion a tendance à se rapprocher de l'arête du dièdre formé par les deux ions CO_3.

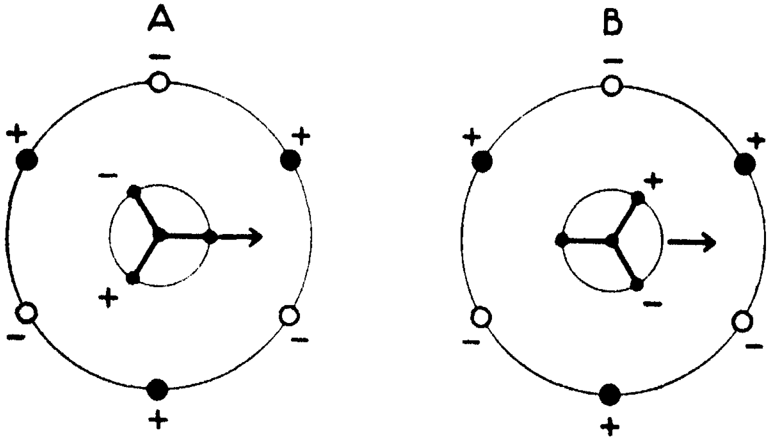

Fig. 7.

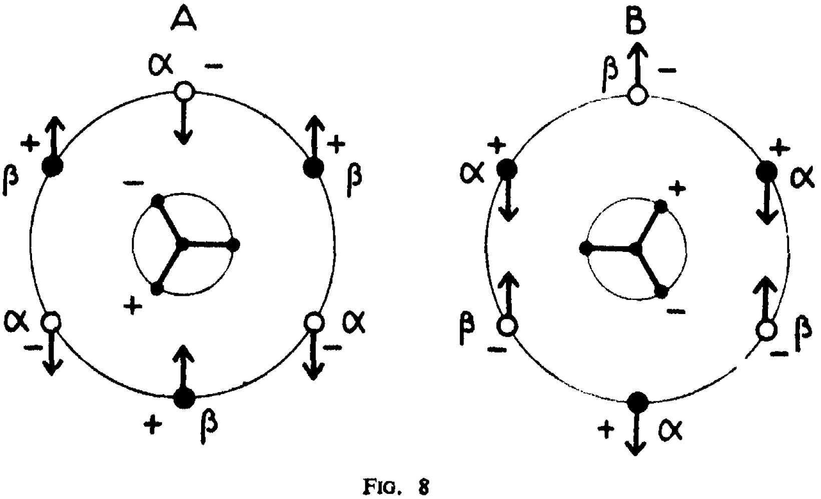

Fig. 8

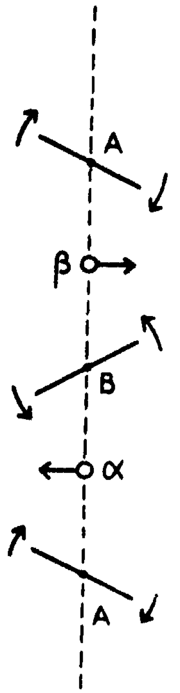

FIG. 9

Le fait que le pivotement E_u est couplé d'une part avec la translation $E_u(1)$ et d'autre part avec la translation $E_u(2)$ montre que ces deux translations sont couplées ensemble et ne peuvent s'effectuer séparément (remarquons que les mouvements de translation $E_u(1)$ et $E_u(2)$ qui se couplent ainsi s'effectuent à angle droit l'une de l'autre). Nous avons donc à faire ici à un couplage triple, et nous prèvoyons trois oscillations réelles de classe E_u formées chacune des trois composantes idéales de cette classe. La participation de la translation $E_u(1)$ confère à ces trois oscillations l'activité infrarouge; la mesure de l'intensité relative des bandes d'absorption infrarouges permettra d'évaluer la participation de la composante $E_u(1)$ à chacune de ces oscillations. Pour la calcite, ces oscillations correspondent aux fréquences d'absorption 106 cm.$^{-1}$, 182 cm.$^{-1}$, 330 cm.$^{-1}$, pour NO_3Na aux fréquences 71 cm.$^{-1}$, 133 cm.$^{-1}$, 217 cm.$^{-1}$

Les considérations précédentes montrent que si la subdivision des oscillations externes en oscillations de translation (cisaillement) et en oscillations de rotation (pivotements) est commode, elle ne peut correspondre qu'à des mouvements idéaux limites. Les oscillations réelles sont constituées par des couplages entre ces formes idéales. La seule subdivision rigoureuse des oscillations fondamentales d'une maille est celle en classes de différentes symétrie, et il convient de remarquer que seuls des formes idéales de même classe de symétrie peuvent se combiner ensemble. Lorsqu'une classe de symétrie ne contient qu'un seul mode idéal de mouvement celui-ci apparaît à l'état pur comme oscillation réelle. C'est le cas de l'oscillation de translation A_{1g} de la calcite.

Des considérations analogues peuvent s'appliquer à d'autres types de cristaux, au type ' aragonite ' par exemple, et permettront de rendre compte du nombre de fréquences actives observées en spectrographie Raman et en spectrographie infrarouge, et de leurs caractères de polarisation.

Sur l'effet Raman des monocristaux en lumière polarisée nous possédons actuellement des données nombreuses qui s'enrichissent constamment par les travaux de plusieurs équipes. Mais sur les spectres d'absorption et de réflexion de ces cristaux dans l'infrarouge lointain nous ne disposons que de données anciennes, incomplètes et peu précises. Il serait très désirable que ces études infrarouges soient reprises en lumière polarisée et avec une grande dispersion. La connaissance précise des fréquences des oscillations externes des réseaux cristallins et des intensités des raies d'absorption et de diffusion qui leur correspondent nous fournira des données intéressantes pour aborder le calcul des forces de liaison qui s'exercent entre les éléments constitutifs des réseaux cristallins.

Nous avons envisagé, jusqu' à présent, uniquement des couplages entre oscillations principales de fréquences finies (branches optiques). Mais il est facile de montrer qu'il doit y avoir aussi certains couplages entre les translations des centres de gravité de la branche acoustique et les mouvements de pivotement.

Considérons, comme exemple simple (Fig. 10), un réseau linéaire de molécules planes, dont les plans sont perpendiculaires au plan de la figure,

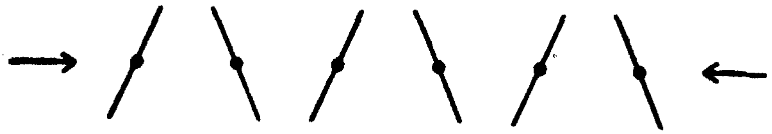

FIG. 10

et qui sont inclinées alternativement des deux cotés de la verticale. Il est évident qu'une compression longitudinale va redresser les plans moléculaires alors qu'une dilatation va les aplatir (mouvement d'accordéon). Une onde de compression-dilatation produira des effets analogues dans des cristaux réelles à trois dimensions formées de molécules planes d'orientation diverses (c'est le cas des cristaux de substances aromatiques). Les ondes thermo-élastiques de basse fréquence des cristaux provoqueront donc des changements d'orientation des éléments constitutifs anisotropes, et ceux-ci se manifesteront par une dépolarisation appréciable des composantes Brillouin de la raie Rayleigh.

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THE FARADAY EFFECT AND MAGNETO-OPTIC ANOMALY OF SOME CUBIC CRYSTALS

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THE magnitude of the Faraday rotation in most transparent substances is expressible by a formula of the Becquerel type, *viz.*,

$$V = \gamma (e/2mc^2) \lambda dn/d\lambda$$

where V is the Verdet constant, e and m are the electronic charge and mass respectively, c the velocity of light, λ the wavelength and n the refractive index. γ is a multiplying factor (called the magneto-optic anomaly) which is approximately constant throughout the visible and the ultra-violet regions, provided the contribution made to the dispersive power by the infra-red absorption bands is eliminated from the formula. Becquerel (1897) arrived at his original formula, in which the factor γ had a value of unity, purely from classical considerations. Van Vleck (1932) has considered the derivation of the Becquerel formula from quantum mechanical ideas and arrives at a conclusion that the value of γ depends on the state of the electrons of an atom and it need not necessarily have a value equal to one. He also found that for atoms and ions in which the electrons have an inert gas configuration (*viz.*, when the outer electrons are in the s state), the value of γ must be equal to unity, *i.e.*, the anomaly disappears. Surprisingly enough, (as has been remarked by Darwin and Watson (1927), such crystals like NaCl and.KCl which are reputed to be of the ionic type have a value of γ of about 0·8. This decrease in γ must obviously be due to the distortion of the electron atmospheres of the atoms due to the crystal structure. The value of γ may be therefore tentatively assumed to be an indication of the departure of the binding from the true ionic type. A study of the magneto-optic rotation and anomaly in crystals would throw considerable light on the nature of the binding in the crystalline state. Accordingly the present writer made some measurements in diamond, zinc blende, and other crystals (Ramaseshan, 1946, 1947). The present work was undertaken with a view to get more accurate data in the case of the crystals already investigated and to extend the studies to other crystals. The Faraday rotation measurements were made in a series of cubic crystals (NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, $NaClO_3$, KAl $(SO_4)_2$ 12 H_2O and NH_4Al $(SO_4)_2$ 12 H_2O and the magneto-optic anomaly has been calculated in each case. To get a clearer insight into the meaning of the magneto-optic anomaly, the Verdet constant and γ for concentrated solutions of these crystals in water have also been determined and the results are reported in this paper.

2. EXPERIMENTAL METHODS

For measurements of the Faraday effect, a polarimeter made by Franz Schmidt and Haench and Co., Berlin, was used. The analyser was mounted on a divided circle that could read upto 0·01°. The polarimeter was fitted with a Lippich double field polariser in which the half shadow angle could be varied from 0° to 20°. When this angle was between 3° and 4° most accurate and satisfactory results were obtained. With clear transparent crystals or solutions repeated settings of the match-point do not vary by more than 0·02°. While taking measurements, the usual precautions that are necessary to eliminate instrumental errors were taken. Each value given in the tables is a mean of ten settings. The sources of light used in these visual measurements were a sodium lamp with a light yellow filter for λ 5893 and a mercury point-o-lite lamp with suitable filters for isolating λ 5461 λ 4358.

On account of the low sensitivity of the eye to the region below λ 4358, visual observations could not be extended below this wavelength. Instead a spectrographic method was resorted to. With the same polarimeter arrangement as mentioned above, the light coming out of the analyser was focussed by means of an achromatic lens on the widened slit of a Hilger baby quartz spectrograph. A series of photographs was taken with different settings of the analyser. Each line in the spectrum being an image of the half shade, the match-point for different wavelengths could be easily determined. It was found that with a half shadow angle of 6° and with a point-o-lite mercury lamp running at 2·4 amps. as the source, an exposure of 30 seconds was sufficient to record the spectral line at the match-point when it is least intense. The analyser was rotated by 0·05° between successive photographs and the match point could be placed within 0·05° to 0·10°; and as the magnetic rotation was usually above 10° the accuracy obtained was quite satisfactory. The extinction positions for the wavelengths λ 5780, λ 5461, λ 4358, λ 4046 and λ 3665 were determined for each crystal without the magnetic field and with the magnetic field on and reversed. The values obtained for the first three wavelengths did not differ by more than ½ to 1% from the values obtained by visual measurements.

These measurements could not be extended beyond λ 3665, since the absorption of the film of canada balsam in the double field polariser became considerable below this wavelength. It is proposed to extend these studies to the far ultraviolet (at least upto λ 2537) by using ultra-violet polarising prisms.

The magnet used in these experiments was of the Rutherford type fitted with special pole-pieces. With currents upto 6 amps. the magnet could be run continuously for an hour without much heating. The refractive indices of the crystals and solutions were measured with a Pulfrich refractometer. The measurements were always made at room temperature (25 ± 1° C.).

3. MATERIALS STUDIED

The crystals whose Verdet constants are to be measured by the above method must be absolutely free from birefringence, since irregular birefringence induced by residual strain would make it impossible to match the two halves of the double field polariser. Further, magnetic rotation as measured by the usual method is known to diminish in the presence of a small amount of birefringence. Therefore, great care was taken to see that only isotropic crystals were chosen for these measurements. A piece of rock-salt about 2 cm. × 2 cm. × 0·8 cm. was cleaved from a larger specimen. The potassium chloride, sodium chlorate, potassium alum and ammonium alum were grown by the method of slow evaporation from saturated solutions. Crystals of ammonium chloride and bromide were grown from saturated solutions in which urea was introduced as an impurity catalyst. Refractive index measurements show that the urea present in the crystals obtained in this way could not be more than 1%. A large crystal of potassium bromide 7·5 cm. × 6·10 cm. × 3·05 cm. in size was used. Although the crystal was full of irregular birefringence there was a small region 3 mm. × 3 mm. where the light was always extinguished when observed between crossed nicols. The surfaces of all the crystals were polished with rouge and putty powder so that the half-shade could be seen through them very clearly.

The solutions were prepared from the purest chemicals manufactured by either Kahlbaum or Merck. In the measurement of the Faraday rotations in solutions, the same glass cell was used for all the solutions.

4. RESULTS

Tables I to IX give the values of the Verdet constant determined for different wavelengths for crystals of NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, $NaClO_3$, $KAl(SO_4)_2\,12H_2O$ and $NH_4Al(SO_4)_2\,12H_2O$. The thickness of the crystal used, the magnetic field and the specific gravity of the crystal are

TABLE I

Magneto-optic data for NaCl crystal

Thickness 2·231 cm. Magnetic field 8450 oersteds
Specific gravity 2·163

Wavelength in Angstroms	2ρ Magnetic rotation in degrees	V Verdet constant in min./cm. oersted		γ%
		Author	Mayer & Landau	
5893	21·68	0·0345	0·0328	89·0
5780	23·06	0·0367	..	89·8
5461	25·76	0·0410	0·0390	90·1
4358	43·00	0·0685	0·0655	88·0
4046	50·80	0·0809	0·0775	89·0
3665	69·70	0·111	0·106	90·0

TABLE II

Magneto-optic data for KCl crystal

Thickness 0·965 cm. Magnetic field 9780 oersteds.
Specific gravity 1·988

λ	2ρ	V		γ%
		Author	Mayer	
5893	8·64	0·0275	0·0267	82·1
5780	9·08	0·0289	..	82·1
5461	10·32	0·0328	0·0316	82·2
4358	17·30	0·0551	0·0534	82·7
4046	21·40	0·0680	..	83·1
3665	27·40	0·0870	..	83·2

TABLE III

Magneto-optic data for KBr crystal

Magnetic field 3540 oersteds Specific gravity 2·75

λ	2ρ		V	γ%
	Thickness 6·10 cm.	Thickness 3·05 cm.		
5893	30·60	15·40	0·0425	78·5
5461	36·00	18·10	0·0500	79·5
4358	60·4	30·15	0·0840	78·2
4046	..	38·00	0·106	79·4
3665	..	48·20	0·134	79·1

TABLE IV

Magneto-optic data for KI crystal

Thickness	1·070 cm.	Magnetic field	8450 oersteds
Specific gravity	3·13		

λ	2ρ	V	γ%
5893	21·10	0·070	78·2
5461	25·00	0·083	78·9
4358	45·50	0·151	78·3

TABLE V

Magneto-optic data for NH_4Cl crystal

Thickness	0·900 cm.	Magnetic field	9780 oersteds
Specific gravity	1·529		

λ	2ρ	V	γ%
5893	10·62	0·0362	71·9
5461	12·61	0·0430	72·7
4358	21·68	0·0739	72·9

TABLE VI

Magneto-optic data for NH_4Br crystal

Thickness	0·746 cm.	Magnetic field	9780 oersteds
Specific gravity	2·325		

λ	2ρ	V	γ%
5893	12·28	0·0504	69·0
5461	14·61	0·0601	69·8
4358	25·29	0·1040	69·5

TABLE VII

Magneto-optic data for $NaClO_3$ crystal

Thickness 2·054 cm. Magnetic field 8 50 oersteds
Specific gravity 2·490

λ	2ρ	V		γ%
		Author	Voigt	
5893	4·68	0·0081	..	31·0
5780	5·02	0·0087	0·0088	31·2
5461	6·08	0·0105	0·0106	31·5
4358	9·40	0·0163	..	31·2
4046	11·60	0·0201	..	32·0
3665	15·80	0·0272	..	33·0

TABLE VIII

Magneto-optic data for potassium alum

Thickness 0·931 cm. Magnetic field 9940 oersteds
Specific gravity 1·76

λ	2ρ	V	γ%
5893	3·82	0·0124	53·3
5780	4·01	0·0130	54·2
5461	4·44	0·0144	55·1
4358	6·78	0·0220	55·5

TABLE IX

Magneto-optic data for ammonium alum

Thickness 0·895 cm. Magnetic field 9940 oersteds
Specific gravity 1·64

λ	2ρ	V	γ%
5893	3·79	0·0128	54·3
5780	3·97	0·0134	54·7
5461	4·48	0·0151	55·2
4358	6·87	0·0232	55·4

also given at the top of each table. The values of the Verdet constant determined by other authors (Mayer, 1909; Landau, 1908; Voigt, 1908) have also been included in the tables. The refractive index data are not given here as they correspond to the values determined by previous workers (Soret, 1884; Haase, 1927; Ramaseshan, 1947). The last column in each table gives the value of γ, the magneto-optic anomaly, expressed as a percentage. Table X gives the natural and magnetic rotations in $NaClO_3$ crystal as also the ratio of the two for different wave-lengths. Table XI gives the concentration, specific gravity, Verdet constant and the magneto-optic anomaly for all the solutions that were studied and Table XII gives their dispersion data.

TABLE X

Natural and magnetic rotations in $NaClO_3$

Thickness of the crystal 2·054

λ	ρ (natural) in degrees/cm.	$\rho \times 10^4$ in degrees/cm. oersted	$\frac{\rho_n}{\rho_m} \times 10^{-4}$
5893	31·4	1·35	23·3
5780	33·2	1·45	23·0
5461	37·0	1·75	21·1
4358	59·2	2·71	21·9
4046	68·2	3·35	20·4
3665	86·0	4·53	18·9

TABLE XI

Magneto-optic data for solutions

Magnetic field 8450 oersteds $\lambda = 5461$ A

Thickness of the column 1·767 cm.

Substance	No. of gms. in 100 gms. water	Sp. Gr.	2ρ	V	γ %
Water ..	..	1·00	7·71	0·0155	76·3
KCl ..	21·2	1·114	9·12	0·0183	79·1
KBr ..	48·78	1·288	11·30	0·0227	85·4
KI ..	88·10	1·476	17·08	0·0343	85·4
NaCl ..	24·12	1·136	9·72	0·0195	79·4
NH_4Cl ..	27·20	1·061	9·98	0·0200	78·8
NH_4Br ..	75·08	1·297	13·68	0·0275	83·2
$NaClO_3$ ..	106·3	1·442	8·61	0·0173	72·9
$KAl(SO_4)_2\,12H_2O$ ..	12·68	1·051	7·86	0·0158	75·5

TABLE XII

Dispersion data for solutions

Substance	n_{5893}	n_{5461}	n_{4358}	$\lambda \frac{dn}{d\lambda}$(5461)
Water ..	1·33239	1·33381	1·33940	2011
KCl ..	1·35594	1·35756	1·36411	2294
KBr ..	1·37771	1·37957	1·38764	2634
KI ..	1·41660	1·41941	1·43159	3979
NaCl ..	1·36462	1·36634	1·37335	2435
NH_4Cl ..	1·37230	1·37408	1·38138	2520
NH_4Br ..	1·40915	1·41146	1·42127	3271
$NaClO_3$ ..	1·38739	1·38905	1·39593	2351
$KAl(SO_4)_2 12H_2O$	1·34304	1·34447	1·35036	2048

5. DISCUSSION OF RESULTS

The tabulated results reveal many interesting features. For instance, one notices that the modified Becquerel formula is very nearly obeyed by all the crystals in the wavelength region between λ 5893 and λ 3665 and the values of γ for each crystal is approximately constant in this region of the spectrum. It is significant that in the case of crystals, γ (NaCl) $>$ γ (KCl) and γ (KCl) $>$ γ (KBr) $>$ γ (KI) and similarly γ (NH_4Cl) $>$ γ (NH_4Br). If it is assumed that the reduction in the value of γ is an indication of the distortion of the electron atmospheres of the ions in the crystal, then heavier ions distort the electron atmospheres more than the lighter ones. The low value of γ for $NaClO_3$ and the alums is probably due to the fact that the covalent linkages in ClO_3 and SO_4 ions produce a very great distortion in the electron atmospheres of the atoms. The comparatively lower values of γ for NH_4Cl and NH_4Br may also be due to the covalent nature of the N–H bond.

Table XIII gives the γ values for the different crystals and solutions.

TABLE XIII

Magneto-optic anomaly in crystals and solutions

Substance	Concentration No gm./100 gm. solution	γ (solution)%	γ (crystal)%
Water ..	100·0	76·3	..
NaCl ..	19·4	79·4	89
KCl ..	17·5	79·1	82
KBr ..	32·8	85·4	79
KI ..	46·8	85·4	78
NH_4Cl ..	21·4	78·8	72
NH_4Br ..	42·9	83·2	69
$NaClO_3$ ..	51·5	72·9	32
$KAl(SO_4)_2 12H_2O$	11·3	75·5	54

Excepting in the case of $NaClO_3$ and potassium alum (the two crystals having very low γ values), the γ for the solutions is always greater than that for water. Of special significance is the fact that γ values for KBr, KI, NH_4Cl and NH_4Br solutions are greater than the corresponding values for the crystals. This indicates that the γ for the ions in solution is greater than that for the ions in the crystal. Tentative calculations show that γ for the ions in solution is between 95% and 100%, *i.e.*, they approach the value suggested by Van Vleck for free ions with inert gas configurations. These calculations and conclusions are purely tentative, as the effects of the ions in solution on the dispersive power of water have not been taken into consideration.

The results obtained with $NaClO_3$ solution are very striking. While the γ in the crystal is only 33%, the γ for a 50% solution shoots upto 72%, *i.e.*, only 4% less than that for water. In fact, if the γ value for the ions in solution were the same as that for the ions in the crystal, then γ for a 50% solution should be of the order of 50%. On the other hand, if the γ for Na ion is assumed to be 100%, then approximate calculations show that γ for ClO_3 ion is of the order of 50 or 60%. The low value of 33% obtained in the $NaClO_3$ crystal is most probably due to partial covalent forces that come into play in the crystal.

In conclusion, the author wishes to thank Prof. Sir C. V. Raman and Prof. R. S. Krishnan for the keen interest they took in these investigations.

SUMMARY

Using a Lippich double field polarimeter together with a spectrograph, the Faraday rotation for crystals of NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, $NaClO_3$, $KAl(SO_4)_2\,12\,H_2O$ and $NH_4Al(SO_4)_2\,12\,H_2O$ have been measured for the wavelengths, λ 5893, λ 5780, λ 5461, λ 4358, λ 4046 and λ 3665. The magnetic rotation for concentrated solutions of these crystals in water were also measured. The magneto-optic anomaly for the crystals and solutions has been calculated from the measurements of the dispersion values. It is found that in the case of crystals, $\gamma(NaCl) > \gamma(KCl) > \gamma(KBr) > \gamma(KI)$ and $\gamma(NH_4Cl) > \gamma(NH_4Br)$. The γ for the solutions except in the case of $NaClO_3$ and the alums is always greater than that for water. The γ values for the ions in solution are higher than those for the ions in the crystal. The presence of covalent bonds tends to diminish the value of γ [$\gamma(NaClO_3$ crystal$) = 33\%$ and $\gamma(\text{Alum}) = 52\%$]. The γ value for a 50% solution of $NaClO_3$ is 72%.

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THEORETICAL EVALUATION OF THE ACOUSTIC WAVE-VELOCITIES IN DIAMOND

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1. INTRODUCTION

STUDIES on the scattering of light in crystals yield data of two distinct types which may enable us to evaluate the acoustic wave-velocities in the solid. In the first place, we observe in the scattered light small spectral shifts, which, following L. Brillouin, have been interpreted as Doppler shifts of frequency arising in the reflection of the incident light waves by sound waves of thermal origin. This interpretation, however, ignores the possible influence of the presence of an external boundary in the crystal on the types of stationary elastic vibrations. It has been suggested (Raman, 1948) that the discrepancies noticed between the facts as actually observed and those theoretically expected according to the assumptions of Brillouin (Krishnan, 1947), are to be explained in this manner. The second method available for the evaluation of the acoustic wave-velocities in the crystal is purely theoretical. It is based on the knowledge of the forces acting between the various constituent atoms, the latter being themselves found out from the Raman effect data. A method has been recently worked out (Ramanathan, 1947) which enables these forces to be evaluated from the observed frequencies of the normal modes of vibration of the crystal. Using the force-constants thus evaluated, one may proceed to calculate the frequencies of stationary elastic vibrations of different types and of various wavelengths. When the latter are sufficiently large, the product of the frequency of the vibration and its wavelength reaches a constant value which is the acoustic wave-velocity in the crystal for the particular direction. We shall proceed to find out the acoustic wave-velocities in diamond in different directions using the procedure indicated and compare the same with the experimentally determined sound-velocities.

2. DESCRIPTION OF THE METHOD

We shall here consider the three principal directions, *viz.*, cubic, dodecahedral and octahedral, and calculate the velocities of transverse and longitudinal stationary vibrations along these in diamond. In the cubic and dodecahedral directions, the carbon atoms in this crystal are arranged in equidistant layers spaced at intervals of 0·89 A.U. and 1·259 A.U. respectively. However, the spacing of the layers of atoms perpendicular to any octahedral direction is alternately greater and smaller, the distance between any two equivalent layers being 2·055 A.U. In the two former cases, the nodal planes must necessarily be located in a plane of atoms along the cubic and dodecahedral directions respectively. Consequently, only such vibrations are possible whose wavelengths are even multiples of the lattice spacing d. Further, if the displacements of the atoms in any plane are assumed to vary harmonically with its distance from the nodal plane, it is found that the equations of motion of all the atoms in the entire crystal are simultaneously satisfied, showing thereby that these are possible modes of elastic vibration in the crystal. This result is found to be valid whether the displacements of the planes of atoms are transverse or longitudinal.

Considering now the cube directions, only two distinct types of vibrations are possible, one longitudinal and one transverse. Along any dodecahedral direction however, three distinct types of vibration are possible, in one of which the planes move normal to themselves while in the other two, they move tangentially with respect to themselves, the direction of motion being along a cube axis or along another dodecahedral direction.

In the case of the octahedral planes, if we assume any two nearly-spaced layers to move always with the same phase and further if the displacements of the double-layers (nearly-spaced layers) are supposed to vary harmonically from any nodal plane which is also another double-layer, then, the equations of motion of all the atoms in the crystal are simultaneously satisfied. There will be two kinds of such vibrations, one longitudinal and the other transverse. Here again, as in the cubic case, there is only one distinct transverse vibration.

Let us suppose that the planes of rest are separated by n oscillating planes which vibrate with their phases opposite on either side of a nodal plane. Then, if d denotes the lattice spacing, the wavelength of the stationary vibration is $\lambda = 2d(n+1)$. The phases and amplitudes of motion of all the atoms in a particular plane will be the same, while, it will be different for atoms in different planes. The displacement ξ_k of any atom in plane k at an instant of time t is given by $\xi_k = \xi \sin \frac{\pi k}{n+1}$, where ξ is the displacement at the antinode. The equation of motion of any atom in plane k is

$$m \frac{d^2\xi_k}{dt^2} = a\xi_k + b(\xi_{k-1} + \xi_{k+1}) + c(\xi_{\cdot-2} + \xi_{k+2}) + d(\xi_{k-3} + \xi_{k+3}) + \ldots\ldots (1)$$

where m is the mass of the carbon atom, a represents the sum of the forces acting on the atom under consideration due to the displacements of all the atoms in the kth layer, b the sum of the forces acting on the atom due to the displacements of all the atoms in the $(k-1)$st or $(k+1)$st layer (these two will be equal), c the sum of the forces on the atom due to the displacements of atoms in $(k-2)$nd or $(k+2)$nd layer, etc. There will be n equations of motion corresponding to $k = 1, 2, 3, \ldots . n$. All the n equations become identical on eliminating ξ_k and expressing them in terms of ξ, the equation obtained being

$$m \frac{d^2\xi}{dt^2} = \Big(a + 2b \cos \frac{\pi}{n+1} + 2c \cos \frac{2\pi}{n+1} + 2d \cos \frac{3\pi}{n+1} + \ldots\ldots\Big) \xi \qquad (2)$$

Or, if ν_n, v_n and λ_n represent respectively the frequency of vibration of the atoms, velocity and wavelength of the stationary elastic vibration, then

$$4\pi^2 m \nu_n{}^2 = \frac{4\pi^2 m v_n{}^2}{\lambda_n{}^2} = a + 2b \cos \frac{\pi}{n+1} + 2c \cos \frac{2\pi}{n+1} + 2d \cos \frac{3\pi}{n+1} + \quad \ldots . \qquad (3)$$

3. EVALUATION OF THE CONSTANTS

In formula (3), when n becomes large and tends to be infinite, the frequency ν_n tends to be zero and the expression on the right-hand side also tends to be zero. Also, the value of the expression $(a + 2b + 2c + 2d + \ldots .)$ which represents a translation of the crystal, is zero. Therefore, an accurate evaluation of the limiting value of the velocity will involve a knowledge of the exact values of the constants a, b, c, d and the other constants representing the series.

In a recent paper already referred to (Ramanathan, 1947), expressions for the frequencies of the nine normal modes of vibration of diamond, were derived in terms of eight force-constants P, Q, R, S, U, W, Σ and Ω, which take account of the influence on each carbon atom of the 28 nearest of its neighbours. A description of these constants and the method of arriving at them by applying the principles of symmetry, are described in the above paper. Also, numerical values for the constants are given there, calculated from the known spectroscopic data.

The constants a, b, c, d, etc., of formula (3) represent, as have been defined already, *the sum of the forces* due to the displacements of *all the atoms* in the plane or planes which they represent. An exact evaluation of these will therefore require also a knowledge of the forces of interaction between atoms in distant planes as well as distant atoms in neighbouring planes. But, at present, since we have no knowledge of these distant forces of interaction, we shall have to be satisfied with those which we know, *viz.*, P, Q, R, S, U, W, Σ and Ω and evaluate a, b, c, etc., in terms of these. It must be remarked here that the distant forces are not likely to play any sensible part in determining the frequencies of the eigenvibrations of the crystal, because, in these the phases of vibration go on alternating at each successive equivalent layer and so there will be a tendency for these forces to cancel out each other. On the other hand, in the case of elastic vibrations of large wavelengths, there will be mass movements of atoms in a very large number of neighbouring planes all moving in the same direction, and therefore, the distant forces of interaction, though of small magnitude, work together and may be expected to have an appreciable effect on the frequency of vibration.

The constants a, b, c, etc., calculated from P, Q, R, etc., satisfy the condition that a translation involves no energy ($a + 2b + 2c +$ etc. $= 0$) because the latter have been made to satisfy this condition in the paper referred to already.

4. RESULTS

I. Cubic Planes: Longitudinal.

The values of the constants can be easily written down from an examination of a model of diamond.

$a = \mathrm{P} + 4\mathrm{S} = 7{\cdot}33 \times 10^5$ dynes per cm.
$b = 2\mathrm{Q} + 4\Sigma = -\,3{\cdot}018 \times 10^5$,,
$c = 4\mathrm{U} = -\,0{\cdot}525 \times 10^5$,,
$d = 2\Sigma = -\,0{\cdot}12 \times 10^5$,,

The value of the velocity increases gradually as we consider vibrations of larger and larger wavelengths and finally reaches a constant value (v_{lim}) which, in this case, is 15900 metres per second.

II. Cubic Planes: Transverse.

$a = \mathrm{P} + 4\mathrm{U} = 6{\cdot}826 \times 10^5$ dynes per cm.
$b = 2\mathrm{Q} + 4\Sigma = -\,3{\cdot}018 \times 10^5$,,
$c = 2\mathrm{S} + 2\mathrm{U} = -\,0{\cdot}272 \times 10^5$,,
$d = 2\Sigma = -\,0{\cdot}12 \times 10^5$,,

$$v_{lim} = 14300 \text{ metres per second.}$$

III. Dodecahedral Planes: Longitudinal.

$a = (\mathrm{P} + 2\mathrm{Q} - 2\mathrm{R} + 2\mathrm{U} - 2\mathrm{W} + 2\Sigma - 2\Omega) = 6{\cdot}122 \times 10^5$ dynes per cm.
$b = (\mathrm{Q} + \mathrm{R} + 2\mathrm{S} + 2\mathrm{U} + 3\Sigma + 3\Omega) = -\,2{\cdot}685 \times 10^5$,,
$c = (\mathrm{U} + \mathrm{W} + 2\Sigma - 2\Omega) = -\,0{\cdot}375 \times 10^5$,,

The limiting velocity = 18300 metres per sec.

IV. Dodecahedral Planes: Transverse along cube axis.

$$\begin{aligned}
a &= (P + 2Q + 2S + 2\Sigma) &&= 4{\cdot}44 \times 10^6 \text{ dynes per cm.}\\
b &= (Q + 4U + 3\Sigma) &&= -2{\cdot}094 \times 10^6 \quad ,,\\
c &= (S + 2\Sigma) &&= -0{\cdot}125 \times 10^6 \quad ,,
\end{aligned}$$

v_{lim} = 14300 metres per sec.

V. Dodecahedral Planes: Transverse along dodecahedral axis.

$$\begin{aligned}
a &= (P+2Q+2R+2U+2W+2\Sigma+2\Omega) &&= 2{\cdot}254 \times 10^6 \text{ dynes per cm.}\\
b &= (Q - R + 2S + 2U + 3\Sigma - 3\Omega) &&= -1{\cdot}00 \times 10^6 \quad ,,\\
c &= (U - W + 2\Sigma + 2\Omega) &&= -0{\cdot}127 \times 10^6 \quad ,,
\end{aligned}$$

v_{lim} = 10900 metres per sec.

VI. Octahedral: Longitudinal.

$$\begin{aligned}
a &= (P + 3Q - 2R + 2S + 4U\\
&\qquad - 4W + 3\Sigma + 6\Omega) &&= 4{\cdot}668 \times 10^6 \text{ dynes per cm.}\\
b &= \tfrac{1}{2}(Q + 2R + 2S + 4U + 4W\\
&\qquad + 9\Sigma - 6\Omega) &&= -2{\cdot}333 \times 10^6 \quad ,,
\end{aligned}$$

v_{lim} = 22300 metres per sec.

VII. Octahedral: Transverse.

$$\begin{aligned}
a &= (P + 3Q + R + 2S + 4U + 2W\\
&\qquad + 3\Sigma - 3\Omega) &&= 1{\cdot}365 \times 10^6 \text{ dynes per cm.}\\
b &= \tfrac{1}{2}(Q - R + 2S + 4U - 2W\\
&\qquad + 9\Sigma + 3\Omega) &&= -0{\cdot}683 \times 10^6 \quad ,,
\end{aligned}$$

v_{lim} = 12100 metres per sec.

The classical theory of elasticity leads to expressions for the velocities of propagation of longitudinal and transverse waves in a cubic crystal in terms of its three elastic constants C_{11}, C_{12} and C_{44}, and ρ its density. The expressions in the case of the cubic, dodecahedral and octahedral directions are $v = \sqrt{\chi/\rho}$ where χ is the quantity shown in the last column.

Cubic	Longitudinal	C_{11}
Cubic	Transverse	C_{44}
Dodecahedral	Longitudinal	$\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$
Dodecahedral	Transverse	C_{44}
Dodecahedral	Transverse	$\frac{1}{2}(C_{11} - C_{12})$
Octahedral	Longitudinal	$\frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})$.
Octahedral	Transverse	$\frac{1}{3}(C_{11} - C_{12} + C_{44})$.

Theory thus shows that there are two transverse velocities possible for any dodecahedral direction and that one of them is the same as the transverse velocity along a cube direction. It is gratifying to note that the above calculations lead to two different transverse velocities for any dodecahedral direction, and that one of them in which the direction of motion is along a cube axis is the same as the velocity of transverse vibrations along a cube direction. That this agreement is not accidental is shown by the fact that in spite of the two formulæ being different, the phase-wavelengths of the vibrations also being different, the limiting velocities come out to be the same.

The Table below reproduces the velocities of acoustic waves calculated above together with those calculated from the elastic constants of diamond determined experimentally by Bhagavantam and Bhimasenachar (1946). It will be seen that in the case of the longitudinal vibrations the agreement is best for the cubic planes, the calculated value being only about 3% lower than the experimental. For the dodecahedral planes the value obtained is about 4% higher than the value calculated from experimental data, while for the octahedral planes it is about 25% higher. It was already explained in an earlier section that the distant interactions have to be considered to make accurate calculations of the velocity. As will be seen from the calculations above, we have considered in the cubic case, the interaction of three planes on either side of the one under consideration, while in the dodecahedral case we were obliged to consider only two. In the octahedral case, only one set of double-layers on either side of the double-layer under consideration is taken account of. It is probable that a consideration of the influence of some more layers of atoms might yield better results in the latter two cases.

Acoustic wave-velocities in diamond

Oscillating planes	Direction of oscillation	Velocity from force-constants	Velocity from elastic-constants
		metres per sec.	metres per sec.
(100)	[100]	15900	16400
,,	[001] or [010]	14300	10800
$(1\bar{1}0)$	[110]	18300	17700
,,	[001]	14300	10800
,,	$[1\bar{1}0]$	10900	8900
$(1\bar{1}1)$	[111]	22300	17700
,,	$[01\bar{1}]$	12100	9500

The agreement in the case of all the transverse modes is much worse, the discrepancy being nearly 25 to 30% in all the cases. This should also be not surprising in view of the remarks about distant interactions already made in a previous section and in view of the fact that the interaction between any two atoms is large when the displacement in question involves a change in the distance between the interacting atoms and small when it does not involve a change in the distance. Therefore, a transverse vibration is likely to be much more influenced by the interaction of distant atoms in the plane under consideration and in neighbouring planes, than a longitudinal vibration. On the other hand, a longitudinal vibration will be more and more influenced than the transverse by the more and more distant planes.

It can be seen that the velocities calculated from the interatomic force-constants lead to nearly the correct value for C_{11}, too high a value for C_{44} and too low a value for C_{12}.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman, with whom he had many useful discussions.

SUMMARY

A dynamical method has been described for evaluating the acoustic wave-velocities in different directions in a crystal, from the interatomic force-constants. The method, applied to the case of diamond, yields two transverse velocities for the dodecahedral directions, one of them coming out to be the same as the transverse velocity in a cubic direction. These facts are in full accordance with theoretical expectations.

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THE PHOTOELASTIC PROPERTIES OF IONIC CRYSTALS

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Abstract.—Recent photoelastic data are used to obtain values of the change in refractive index with density for a series of cubic crystals. These experimental values are found to be smaller than those calculated from either the Lorentz-Lorenz or the Drude equations. The difference between the experimental and calculated values results from a decrease in the molar polarizability with increase in density. In MgO the change in polarizability is relatively large and the refractive index actually decreases with increase in density while the other crystals show an increase. The decrease in molar polarizability with density as measured by the strain-polarizability, λ_0, can be correlated with the amount of homopolar binding and ion overlap in the crystal. It is suggested that an increase in density increases the amount of homopolar binding and ion overlap. Further information about the dynamic changes in polarizability during vibration of the ions can be obtained from the change in refractive index with temperature at constant density and from Raman spectra.

INTRODUCTION

AS PART of a fundamental investigation of the relation between the properties of non-metallic crystals and their atomic structure, a detailed study is being carried out of the photoelastic, thermo-optic and infrared properties of crystals. During Sir C. V. Raman's visit to the United States the authors had several stimulating discussions with him about this work, which was then in progress, and it is with pleasure that they present the results of some of these investigations as a contribution to this special issue dedicated to him.

Although it is not possible as yet to calculate from fundamental considerations either classically or quantum mechanically the effect of interaction between the atoms in a solid on their polarizabilities, one can obtain considerable information about these interactions from data on the change of refractive index with density $dn/d\rho$ (Mueller, 1935; Burstein and Smith, 1948*a*). The $dn/d\rho$ cannot be measured directly but can be calculated from photoelastic constants. Such data yield information about the change in the average polarizability of the atoms with change in equilibrium interatomic distance resulting from a homogeneous deformation.

BACKGROUND

When an electric field at optical frequencies is applied at the boundaries of an ionic crystal dipole moments are induced in the ions. The effective field at the interior of the dielectric which is acting to polarize the ions is given by

$$E' = E - \frac{4\pi}{3} P + E_L + E_C, \tag{1}$$

where E is the applied electric field; P is the polarization of the medium; $\frac{4\pi}{3} P - E_L$ is the Lorentz-Lorenz field contributed by the surrounding dipoles; and E_C is the Coulomb field contributed by the surrounding ions acting on the displaced charge.

The polarization of the medium is related to the applied electric field by the relation

$$P = \frac{\epsilon - 1}{4\pi} E, \tag{2}$$

where ϵ is the dielectric constant at the frequencies of the applied field.

The dipole moment μ_i induced in an ion of type i is given, to a first approximation, by the linear equation

$$\mu_i = a_i E', \tag{3}$$

where a_i is the polarizability of the i type ion. The μ_i's, E and P are vectors while the a_i's and ϵ are second-order tensors.*

The polarization of the medium can also be defined in terms of the dipole moments induced in the ions by the effective field

$$P = \Sigma N_{Vi} \mu_i = \rho \Sigma N_{Gi} \mu_i, \tag{4}$$

where N_{Vi} is the number of i type atoms per unit volume; ρ is the density and N_{Gi} is the number of atoms per gram.

In cubic crystals the E_L and E_c contributions are zero to a first approximation. The effective field for such crystals is given by

$$E' = E - \frac{4\pi}{3} P \tag{5}$$

and the induced moment is given by

$$\mu_i = a_i \left(E - \frac{4\pi}{3} P \right). \tag{6}$$

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* Only the real part of the polarizability will be considered here since the discussion will be limited to frequencies for which the crystal is transparent.

By combining equations, one obtains the well-known Lorentz-Lorenz equation for the molar polarizability or refractivity of a cubic crystal in terms of the refractive index, n_0,

$$V_M \left(\frac{n_0^2 - 1}{n_0^2 - 2}\right) = \frac{4\pi}{3} N_A \Sigma N_{Mi} \alpha_i = R, \tag{7}$$

where V_M is the molar volume, n_0 is the refractive index, N_{Mi} is the number of i type ions per molecule, and N_A is the Avogadro number.

E_L and E_c do contribute to the effective field in crystals which do not have cubic symmetry and their magnitudes will in general be different along the three principal axes of the crystal. This is also true for deformed cubic crystals where the cubic symmetry of the lattice is destroyed. The magnitude of the L–L and Coulomb fields will depend on the magnitude and type of deformation. The change in refractive index resulting from an elastic deformation will, therefore, depend on the magnitude of these fields and on the change in density.

PHOTOELASTIC THEORY

In developing his theory of photoelasticity Banerjee (1927) took into account the L–L field resulting from the deformation of the cubic symmetry, but neglected the Coulomb field. Following Fajans and Joos (1924) who showed that the polarizabilities of the ions are smaller in the crystal than in the independent gaseous state, Banerjee considered that a further decrease in volume decreased the polarizability still further. He therefore included in his calculations the change in polarizability of the ions with strain but neglected to treat the polarizability as a second-order tensor. In another theoretical treatment Herzfeld and Lee (1933) took into account the Coulomb field as well as the L–L field in the deformed crystal but neglected the change in the polarizability of ions with strain. All three factors; the L–L field, the Coulomb field and the change in polarizability of the ions with strain were properly considered by Mueller (1935) who was able to explain qualitatively the magnitudes and signs of the photoelastic effects of the few crystals whose constants were known at that time. His theory does not permit quantitative predictions of the photoelastic properties since it requires empirical values of the optical strengths and polarizabilities, which are available for only a few crystals and the strain-polarizability constants of the ions which are not available. Mueller's theory is, however, useful for determining the change in polarizability of the ions with strain since there is no way as yet for calculating the strain polarizability constants from fundamental considerations. Given the optical strengths and polarizabilities of the ions one can calculate the L–L and Coulomb contributions by means of this theory. The strain polarizability constants can then be calculated from these contributions and the photo elastic constants.

For the changes in refractive index caused by hydrostatic pressure the theory is considerably simplified since the cubic symmetry of the crystal is maintained and E_L and E_c remain zero. Therefore, one need only consider the changes in the polarizability of the ions with interatomic distance and the change in density. Following Mueller, the change in molar polarizability with strain (homogeneous displacement of the ions) is represented by a set of phenomenological strain polarizability constants λ defined by the relation

$$R = R_0(1 + \lambda S), \tag{8}$$

where R_0 is the molar polarizability for the undeformed crystal; R is the molar polarizability of the deformed crystal and S is the strain. For the higher symmetry cubic crystals there are only three constants λ_{11}, λ_{12}, and λ_{44}, analogous to the strain optical constants p_{11}, p_{12}, and p_{44}. The change in molar polarizability due to a hydrostatic deformation dV/V_M is determined by

$$R = R_0\left(1 + \lambda_0\frac{dV}{V_M}\right) = R_0\left(1 - \lambda_0\frac{d\rho}{\rho}\right) \tag{9}$$

where

$$\lambda_0 = (\lambda_{11} + 2\lambda_{12})/3 \tag{10}$$

The change in refractive index due to a change in density results from a change in the number of ions per unit volume and a change in the polarizability of the ions and is given by

$$\frac{dn}{d\rho} = \left(\frac{\partial n}{\partial \rho}\right)_R + \left(\frac{\partial n}{\partial R}\right)_\rho \frac{dR}{d\rho}. \tag{11}$$

The change in refractive index with change in density calculated from the L–L equation gives the first term in equation (11), since, in deriving the L–L equation, the polarizability of the ions was assumed to be constant and independent of the density. The total change in refractive index with density can be written as

$$\frac{dn}{d\rho} = (1 - \lambda_0)\frac{(n_0^2 + 2)(n_0^2 - 1)}{6n_0\rho} = (1 - \lambda_0)\left(\frac{\partial n}{\partial \rho}\right)_R. \tag{12}$$

The experimental value of $dn/d\rho$ can be calculated from the photoelastic constants p_{11} and p_{12} (Pockels, 1906) by means of the relation

$$\frac{dn}{d\rho} = \frac{n_0^3(p_{11} + 2p_{12})}{6\rho} \tag{13}$$

Values of λ_0 can therefore be calculated from the experimental values of $dn/d\rho$ and the $(\partial n/\partial \rho)$ calculated from the L–L equation.

Using these relations, Mueller calculated the λ_0 for NaCl, CaF_2 and KCl.* Within the accuracy of the data, these crystals were found to have the same λ_0 value (approximately 0·5). On the basis of these results Mueller assumed that other crystals would have similar λ_0 values. Calculations based on recent photoelastic data (Burstein and Smith, 1948) show, however, that λ_0 varies considerably from crystal to crystal and that Mueller's assumption concerning the strain polarizability contribution to the photoelastic constants must also be modified to take into account structure effects.

EXPERIMENTAL DATA

The available data on $dn/d\rho$ calculated from photoelastic data by means of equation (13), $(\partial n/\partial\rho)_R$ calculated from the L–L equation, and λ_0 calculated from these quantities by means of equation (12) are given in Table I. Data for diamond which is completely homopolar are also included.

TABLE I

Crystal	MO	$\rho\left(\frac{dn}{d\rho}\right)_{obs.}$	L—L Equation			Drude Equation		
			$\rho\left(\frac{\partial n}{\delta\rho}\right)_{calc.}$	λ_0	$\frac{\Delta R}{R}$‡	$\rho\left(\frac{\partial n}{\delta\rho}\right)_{calc.}$	λ_0	$\frac{\Delta R}{R}$‡
LiF ..	1·392	0·1	·44	~·7	·16	·34	~·7	−·12
NaCl ..	1·544	0·24	·66	·63	·15	·45	·47	−·26
KCl ..	1·490	0·23	·58	·61	·05	·41	·44	−·29
KBr ..	1·559	0·35	·68	·48	·02	·46	·24	−·38
KI ..	1·667	0·44	·85	·48	·02	·53	·19	−·45
MgO ..	1·736	−·4	·97	~1·4	·76	·52	~1·8	·41
CaF_2 ..	1·434	·25	·50	·50	·02	·37	·32	−·31
Diamond*	2·417	1·24	2·62	·53	..	1·00	·24	..
K-alum†	1·456	·50	·53	·06	..	·38	·31	..

* Ramachandran (1947 *a*), Burstein and Smith (1948 *b*)

† Bhagavantam and Suryanaryana (1947)

‡ The R_r values used to calculate $\frac{\Delta R}{R}$ are taken from Pauling (1927).

The experimental values of $dn/d\rho$ are in every case smaller than the values of $(\partial n/\partial\rho)_R$ calculated from the L–L equation. In MgO an increase in density actually decreases the refractive index; the contribution from the decrease in polarizability of the ions is greater than the contribution from the change in the number of ions per unit volume. MgO is unique in this respect. Of the alkali halides studied thus far, LiF has the largest change in polarizability of the ions with change in density. Diamond, which is completely homopolar, and CaF_2 have λ_0 values which are about the same

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[*] The $dn/d\rho$ for KCl was estimated from dn/dT data.

as those of the alkali halides, while K-alum has the smallest λ_0 of the cubic crystals studied thus far.

DISCUSSION

A physical picture of the significance of λ_0 can be obtained by comparing the molar polarizability of the ions in the gaseous state R_g with that of the ions in the undeformed crystals R_s. The difference in these quantities as measured by $\frac{\Delta R}{R_{AV.}} = \frac{R_g - R_s}{R_{AV.}}$ is also given in Table I. The ΔR corresponds to the overall change in molar polarizability of the ions in going from the independent gaseous state to the solid state and is a measure of the amount of overlapping of the ions in the unstressed solid. The λ_0 then represents the further change in polarizability as the density of the solid is changed. That is, it corresponds to the slope of the relative molar polarizability *vs.* density curve for the solid at a given temperature. This curve is given schematically in Fig. 1 for ionic crystals. The R and λ_0 values are indicated on the curve for crystals in which (*a*) the interaction between the ions is small (ionic bonding, ΔR small and $\lambda_0 < 1$), (*b*) the interaction is appreciable (intermediate ionic and homopolar bonding, ΔR large and $\lambda_0 > 1$) and (*c*) the interaction is complete (homopolar bonding, ΔR large and $\lambda_0 < 1$).

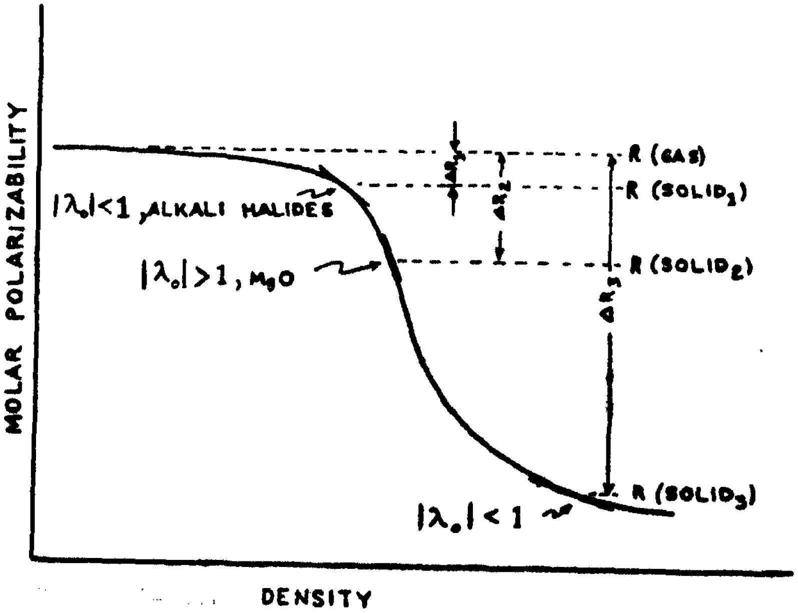

FIG. 1

Fajans and Joos (1924) attributed the change in the polarizability of the ions in going from the gaseous state to the solid state and the non-addivity of the polarizabilities of the ions in solids to Coulomb deformations of the ions by its neighbours. This was indicated by the fact that ions with small radii and large charge produced the largest effects. Mueller (1935), however, has suggested that since a change in molar polarizability is found in homopolar solids, changes in polarizability are due to changes in the energy levels and transition probabilities of the optical electrons.

The new λ_0 data suggest further that the change in polarizability with interatomic distance in ionic crystals is due primarily to a change in the amount of ion overlapping and, therefore, to a change in the relative amount of ionic and homopolar bonding (non-central force interactions between the ions). The magnitude of these changes will, therefore, depend on the amount of overlapping and homopolar bonding already present in the unstressed crystal, which accounts for the large variation in λ_0 from crystal to crystal.

In addition to the change in polarizability due to a change in the character of the bonding, there is also a contribution due to the tightening of shared electrons in homopolar crystals, as shown by the data for diamond and by the calculation on the change in polarizability of the hydrogen molecule with change in interatomic distance (Wang, 1930).

In crystals which contain radicals the interatomic distances within the radicals are not appreciably altered when the crystal is deformed by an external stress. Since the major contribution to R comes from these groups, changes in R with density will be small. This is apparently the explanation for the small λ_0 in K-alum, where the contribution to R comes mainly from the $SO_4^=$ and H_2O groups.

That λ_0 can be correlated with the extent of ion overlapping and homopolar bonding in polar crystals is shown by the data in Table II where they are tabulated for a number of NaCl-type crystals together with other properties known to be associated with homopolar bonding, such as the deviations of the elastic constants from Cauchy relations and the coefficient of expansion. The deviations from the Cauchy relation are a measure of the non-central forces resulting from ion overlapping and homopolar bonding (Löwdin, 1947). Although this does not always show up, as in diamond where the Cauchy relations appear to hold, they are of value when comparing different NaCl-type crystals with one another. Thus we find that the deviation from the Cauchy relations is considerable in both MgO and LiF. Additional evidence for the existence of appreciable overlapping between the ions and homopolar bonding in MgO is found in the calculations of the electron distribution about ions from X-ray scattering data (Wollan, 1930) and X-ray emission band data (O'Brian and Skinner, 1940). Since homopolar bonding in ionic crystals increases the attractive force between the ions and therefore the lattice energy, there will also be a rough correlation between homopolar bonding and such properties as thermal expansion, Debye temperature and melting point. These are also given in Table II.

TABLE II

Crystal	λ_0	C_{44}/C_{12}	$\gamma \times 10^4$	θ°k	Tm.p.°k
LiF ..	·7	1·4	10·2	..	1140
NaCl ..	·63	·9	12·0	280	1070
KCl ..	·61	1·0	11·4	230	1050
KBr ..	·48	1·1	12·0	180	1000
KI ..	·48	1·0	13·5	130	955
MgO ..	1·4	1·8	3·9	770	3070

λ_0 = strain polarizability constant for hydrostatic pressure;
C_{44}/C_{12} = ratio of elastic constants (the Cauchy relations are $C_{44}/C_{12} = 1$);
γ = cubical coefficient of expansion;
θ = Debye temperature;
$T_{m.p.}$ = melting point.

It has been shown from quantum mechanical considerations that the L–L equation is valid only for solids in which the atoms are arranged in a lattice with cubic symmetry and can be treated as harmonic oscillators. Classically this condition is satisfied by point-like ions. It is apparent that as a result of ion overlapping and homopolar binding this condition is not satisfied for the alkali halides. The effective field acting to polarize the ions will not be given simply by equation (5) but will contain additional terms which depend on the amount of ion overlapping and homopolar binding and which will vary from crystal to crystal.* Attempts to derive expressions for the refractive index which take such terms into account lead to expressions which are intermediate between the L–L and the Drude equations. The Drude equation, in which the L–L field is neglected, can be written in the form

$$V_M (n_0^2 - 1) = 4\pi \, N_A \Sigma \, N_{Mi} \, a_i = 3R_D. \tag{14}$$

The λ_0 and $\Delta R/R$ values calculated from dn/dp and $(\partial n|\partial p)_R$ by means of the Drude equation which represents one limiting case are also given in Table I for comparison with those obtained from the L–L equation as the other extreme. The magnitude and sign of λ_0 calculated from the two equations show the same trend. It appears therefore that, although the form of the refractive index equation may influence the magnitude of λ_0 it is still a useful measure of the change in polarizability with density. On the other hand, the values of $\frac{\Delta R}{R}$ calculated from the two equations are quite different. The Drude equation leads to relatively large negative values of $\frac{\Delta R}{R}$ while the L–L equation leads to positive values.* Since λ_0 is positive for the crystals considered here one would expect the $\Delta R/R$ to be positive. This indicates that the proper form of the refractive index equation may be closer to the L–L equation than to the Drude equation.

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* The concept of individual ion polarizabilities loses its meaning in crystals with homopolar bonding. One should use a polarizability of the crystal per unit cell rather than per ion.

CONCLUDING REMARKS

Numerous attempts have been made to fit the data for the refractive index of crystals at different wavelengths into dispersion formulæ. By adjusting arbitrary constants it has been possible to get the different types of dispersion equations into good agreement with the data (Ramachandran, 1947). Since however, the physical validity of the form of the equation cannot be verified, no attempt will be made to discuss the significance of λ_0 in terms of a detailed dispersion equation. Instead, the changes in polarizability resulting from changes in density will be discussed qualitatively in term of the factors which determine the magnitude of the polarizability. For purposes of discussion one need only assume that the combined polarizability of the positive and negative ions can be represented by an equation of the form

$$a = C\,\Sigma\,\frac{f_{0k}}{\nu_{0k}^2 - \nu_k^2}, \tag{15}$$

where ν_{0k} is a dispersion frequency of the crystal and f_{0k} is the corresponding optical strength or transition probability.† This is based on the use of a refractive index equation in which the local field is taken into account. Neglecting the effect of a change in the local field on the calculated λ_0 the decrease in the polarizability of an ion with density can result from a change in either ν_{0k} or f_{0k}. In order to distinguish between the two effects it is necessary to study the change in dn/dp with frequency of the applied field.

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* λ_0 is less affected than is Δ R/R by the form of the equation since it represents the slope of the change in R while Δ R/R depends on the magnitude of R.

† The dispersion frequency corresponds to the absorption frequency of the ions in the absence of the L-L field. The experimentally observed absorption frequency (*i.e.*, when the L-L field is present) is given by

$$\nu_{rk} = \nu_{0k} - \frac{4\pi}{3}\,\frac{Ne^2 f_k}{m}$$

Obviously if the effect is primarily one of wavelength shift the magnitude of dn/dp will depend on the relative position of the dispersion frequencies and the frequency at which the measurements are made. Since the dispersion frequencies for the various crystals are different this may account in part for the variation in the observed values of λ_0.

Although there are no data for the shift in the absorption bands or for changes in the transition probabilities with a change in density, data are available for such changes caused by temperature. Fesefeld (1930) has made a detailed study of the absorption of KI and RbBr in the near ultraviolet as a function of temperature. As the temperature is increased the bands are found to shift toward longer wavelengths and their intensities are decreased. The wavelength shifts for KI calculated from dn/dT data are in agreement with the observed values (Ramachandran, 1947 *b*).

The polarizability of an ion is a function of the instantaneous configuration of the surrounding ions. Since the ions vibrate relative to one another as a result of thermal energy, the polarizability, which is a non-linear function of the interatomic distance will vary periodically in time. The polarizability defined by equation (3) is the time average of the instantaneous values. Its magnitude depends on the non-linear variation of the polarizability with interatomic distance as well as on the value of the instantaneous polarizability of the ions at the equilibrium interatomic distance. The strain polarizability constant λ_0 is a measure of the change in the average polarizability of the ions with change in equilibrium distance.

Information about the instantaneous changes in polarizability of the ions in a crystal during vibration can also be obtained from data on the change in refractive index with temperature at constant density, $(\partial n/\partial T)_\rho$, which is a measure of the change in polarizability of the ions with temperature at constant equilibrium distance and is determined by the change in magnitude of the non-linear terms corresponding to the change in amplitude of vibration of the ions with change in temperature.* Values of $(\partial n/\partial T)_\rho$ cannot be obtained directly but can be calculated by combining data on the total change in refractive index with temperature, dn/dT, with data on dn/dp and thermal expansion.

Still further information about the linear and quadratic changes in polarizability which take place during vibration can be obtained from data on Raman spectra intensities. For crystals with NaCl structure, only second-order Raman spectra are observed since the optical vibrations are symmetrical and the linear changes in polarizability are zero. Measurements on NaCl show that the zero order spectra are quite weak (Krishnan, 1947). Measurements of the intensity of the second-order Raman spectra of MgO and LiF would be of particular value for correlation with λ_0 data.

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* In his papers on thermo-optic properties of solids, Ramachandran (1947 *b*) does not separate the effect of density and the effect of temperature on the polarizability.

The investigation of the photoelastic and thermo-optic properties of crystals and their dependence on temperature is being continued at this laboratory, and is being supplemented by a study of Raman and infrared spectra.

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THE INFRARED PROPERTIES OF MAGNESIUM OXIDE AND THEIR INTERPRETATION

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Abstract.—New determinations of the infrared absorption and reflection curves of magnesium oxide show that these curves do not differ in form from those of other NaCl-type crystals. Detailed comparison of MgO with LiF, NaF, NaCl, and KCl, for which accurate data are available, reveals a correlation between the amount of coupling of vibrational modes and the amount of homopolar bonding and ionic overlapping. It is suggested that the coupling is primarily associated with the change in polarizability of the ions during vibration rather than with anharmonic vibrations as proposed by existing theories.

INTRODUCTION

THE infrared properties of ionic crystals depend on the vibration of the ions relative to one another and thereby on the interaction between these ions. Photoelastic studies (Burstein and Smith, 1948 *a*, *b*) show that an increase in density decreases the refractive index of magnesium oxide as a result of a relatively large decrease in the polarizability of the ions. The alkali halides, on the other hand, exhibit an increase in refractive index and a correspondingly smaller decrease in the ionic polarizabilities when the density is increased. The large change in ionic polarizability in MgO can be attributed to the considerable overlapping of the ions and to the partially homopolar character of their bonding. There is less overlapping of ions in the alkali halides and the bonding is correspondingly more ionic. This is borne out by other evidence for partially homopolar bonding in MgO such as the large deviation of its elastic constants from the Cauchy relations (Durand, 1936). The infrared properties of MgO were therefore investigated in order to see whether they could also be correlated with the overlapping and the partially homopolar bonding of the ions.

Data in the literature on the infrared properties of MgO are incomplete and contradictory. Tolksdorf (1928), studying the transmission of thin films of powdered MgO held between plates of sodium chloride, observed absorption bands at 3·85, 7·65 and 14·2 microns. Strong (1931), using reststrahlen, found that a fumed layer of MgO showed strong absorption in the neighbourhood of 23 μ and that a cleavage plate of MgO showed 80 per cent. reflection at this wavelength. Fock (1934), measuring the transmission of MgO fumed onto nitrocellulose films, found a strong absorption maximum at 17·3 μ with minor maxima at 14·9 and 25 μ.

A more detailed study was then made by Barnes, Brattain and Seitz (1935) (hereafter referred to as B–B–S) of the transmission of thin cleavage plates of MgO, as well as thin films of MgO evaporated under vacuum onto nitrocellulose and layers of MgO fumed onto plates of NaCl. Using a NaCl prism spectrometer, they observed a large number of narrow, weak absorption bands starting at 6 μ. They also obtained a reflection curve for a cleavage plate which showed two sharp reflection peaks at 14·8 and 15·3 μ.

In attempting to explain the complex secondary structure observed by B–B–S in the transmission curves of MgO, Seitz pointed out in the theoretical section of the paper that, since the elastic constants of MgO exhibited considerable deviation from the Cauchy relations, its properties could not be completely calculated from a model using central force interactions between the ions. He, therefore, used a more general potential function and treated the crystal as a three-dimensional, quantum mechanical system of interacting particles. The results of these calculations indicated that the crystal should exhibit a complex absorption spectrum. It was not possible, however, to obtain any correlation of the theory with the experimental data since the position of the fundamental absorption band was not known and since data on the numerous secondary bands were incomplete because of temperature broadening and the low resolving power of the spectrometer employed by Barnes and Brattain.

From the B–B–S data on single crystals it appears that the infrared properties of MgO differ considerably from those of the alkali halides which also have NaCl structures. For example, their MgO reflection curve as reproduced in Fig. 1 contains two adjacent, sharp peaks, whereas curves for the alkali halides show one broad major peak and a narrower minor peak at shorter wavelengths. In addition, their MgO transmission curves (Fig. 2) show considerably more secondary structure than those of the alkali halides in the corresponding wavelength regions.

Examination of the transmission curves obtained by B–B–S showed that the curves for the various thicknesses differed among themselves in the position and appearance of the secondary bands in a manner that did not

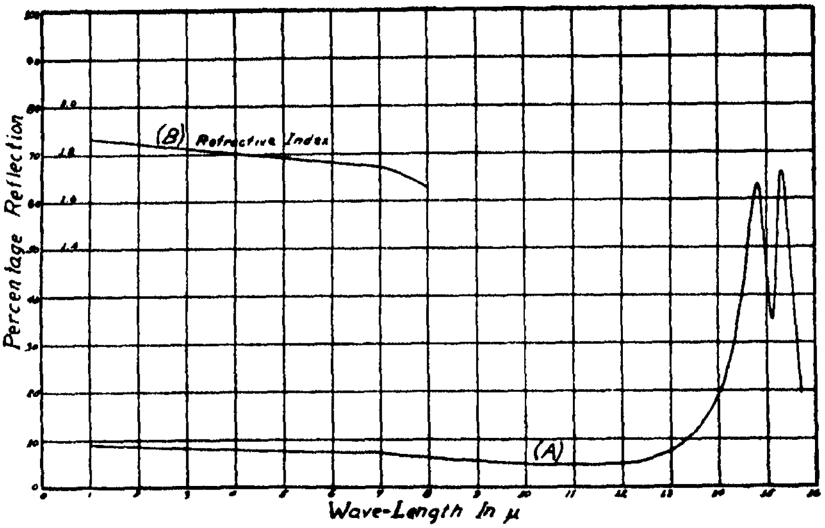

FIG. 1. (A) Reflection of a crystal of MgO ; relative to a silver mirror Barnes, (Brattain and Seitz, 1935).

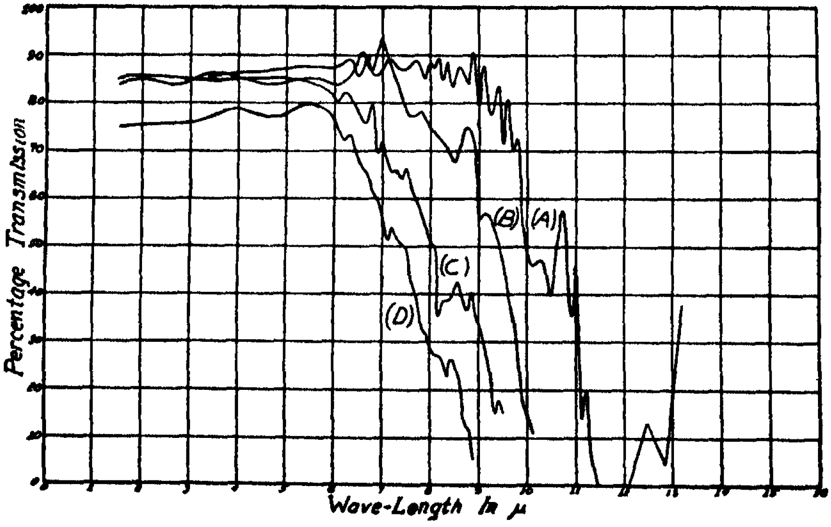

FIG. 2. Transmission of cleaved plates of MgO ; (*a*) 0.12 mm., (*b*) 0.47 mm., (*c*) 1.75 mm., (*d*) 3.05 mm. (Barnes, Brattain and Seitz, 1935).

seem attributable to a thickness factor as suggested by B–B–S. In view of the uncertainty concerning the validity of the B–B–S data and the considerable differences found between MgO and other NaCl-type crystals, it was decided to repeat the measurements and to extend them to longer wavelengths by means of KBr and TlBr–I prisms. Data on the transmission and reflection of cleavage plates of MgO have been obtained at room temperature and the measurements are now being extended to thin films and low temperatures.

EXPERIMENTAL PROCEDURE AND RESULTS

The infrared transmission and reflection measurements were made with Perkin-Elmer spectrometers employing NaCl, KBr, and TlBr–I (Plyler, 1948) prisms and appropriate shutters and reflection filters to minimize errors due to scattered light. Continuous records of the data as a function of wavelength were obtained by means of electronic amplifiers and recorders.

A simple modification of the pre-slit optical system (Fig. 3) was employed for reflection measurements. The image of a globar source is focused at the reflection sample holder at an angle of incidence of 10°. The reflection sample or the aluminum comparison mirror thus acts as a virtual source which is then focused on the entrance slit. Small samples can be used by locating them at a focus in this manner. Either the sample or the aluminum reference mirror can be moved into the beam by means of a simple slide mechanism. The new components (a globar source, concave mirror and sample holder) are mounted on a plate with appropriate cutouts so that it can be put into position without disturbing the original source, plane mirror, and concave mirror that are supplied with the instrument.

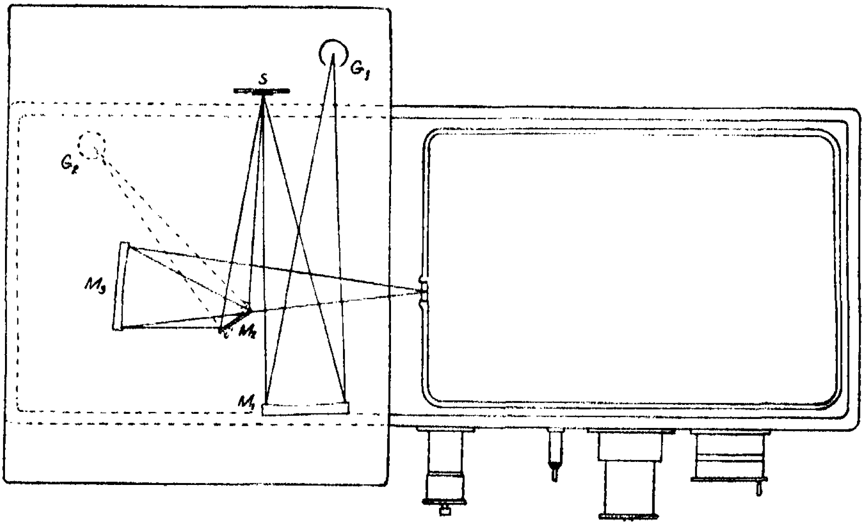

FIG. 3. Schematic layout of modified pre-slit optical system. Full lines indicate new light path for reflection measurements. The components are : G_1 and G_2, globar sources ; M_1 and M_2, concave mirrors ; M_3, plane mirror ; S, sliding holder for sample and reference mirror.

This enables the instrument to be used for either transmission or reflection measurements. In order to change from one type of measurement to the other, it is only necessary to switch the power to the appropriate globar and to rotate the plane mirror (or reflection filter) M_2. The reflection components are also useful for transmission measurements, especially when two reflection filters are required to minimize scattering errors. For this purpose a second reflection filter is placed in the reflection sample holder.

Transmission measurements were made on a series of MgO plates with thicknesses ranging from 0·09 to 9·0 mm. which were cleaved from a number of crystals obtained from The Norton Company, Worcester, Mass, U.S.A. Relative spectral reflection curves were obtained by comparing the reflection from freshly cleaved surfaces of MgO with that from an aluminum mirror. In all cases there was very good agreement between the data obtained with a given sample by the Naval Research Laboratory and the National Bureau of Standards.

Transmission curves of cleavage plates of different thicknesses (0·09 to 9 mm.) at room temperature are given in Fig. 4. Absorption bands are found at 8·3, 10·18, and 11·82 μ and there are indications of very weak

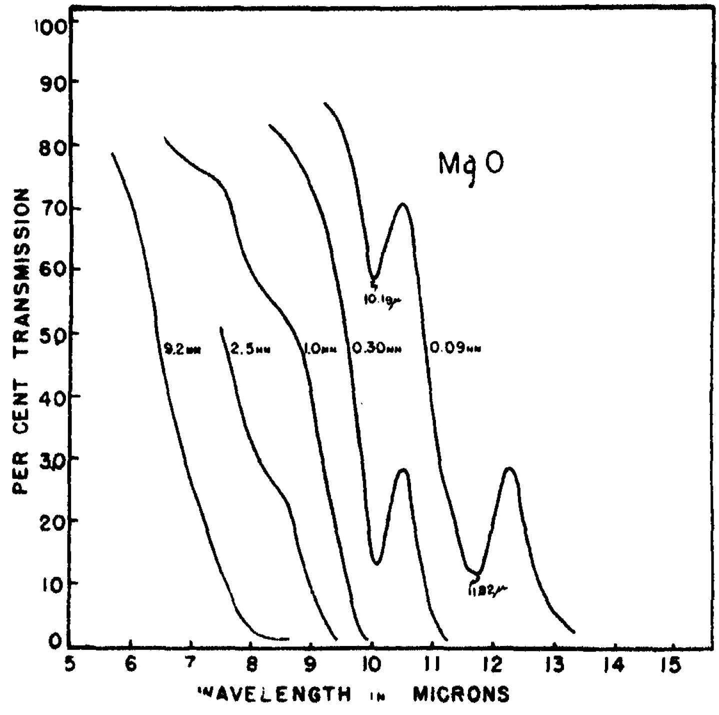

Fig. 4. Transmission of five cleavage plates of MgO.

bands at shorter wavelengths. The absorption bands are broad and not at all like the fine structure observed by B–B–S.

The possibility that these bands may be due to impurities was checked by calculating the absorption coefficient $\left(k = -\frac{1}{d} \ln \frac{I}{I_0}\right)$ from the transmission data for plates cleaved from several original crystals. The values of the coefficient for the different samples were found to agree with one another within the experimental error. On the other hand, large differences in ultraviolet transmission were observed for the different samples in the region of 2,000 to 3,000 Å, indicating that there were considerable differences in impurity content. It is reasonable to conclude from the agreement in the infrared absorption coefficient for the different samples that the bands in the infrared are not due to impurities but to MgO itself.

The reflection curve of a freshly cleaved surface of MgO relative to aluminum is given in Fig. 5. The reflection increases rapidly beyond 13 μ, levels off briefly at about 15 μ and rises again at 16 μ until a peak is reached at approximately 22 μ after which the curve falls off rapidly beyond 24 μ. Data obtained with the NaCl prism in the region of 15·5 μ show a slight dip of a few percent. which is not found when using the KBr prism. This dip can be attributed to the lack of complete correction for scattering since the NaCl prism begins to absorb strongly in this region. Similarly the data

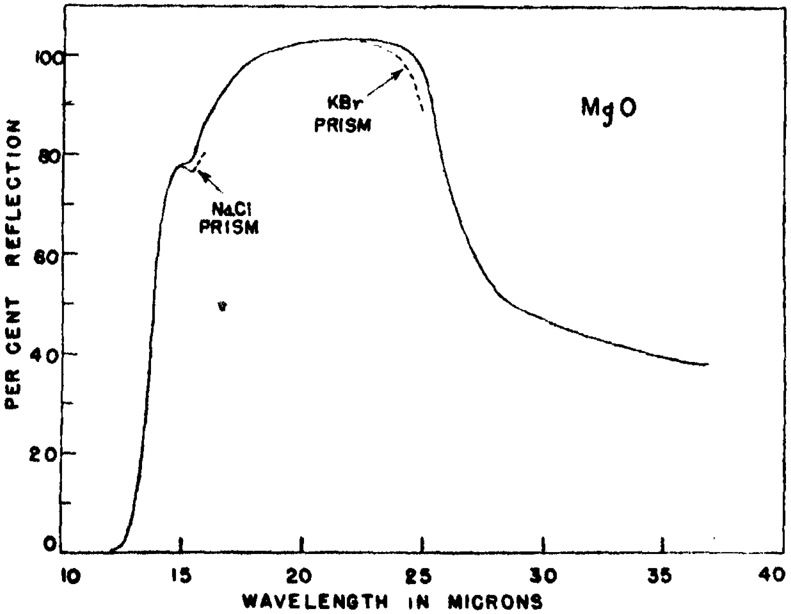

FIG. 5. Reflection curve of MgO cleavage surface relative to an aluminum mirror.

obtained with the KBr prism show lower values above 23 μ than the data obtained with the TlBr–I prism because the scattering error is magnified by the decreased transmission of the KBr prism. Scattering errors do not become appreciable in the TlBr–I prism until a wavelength of 35 μ is reached.

The numerous, narrow secondary bands in the data obtained by B–B–S could be due to errors likely to occur in their point-by-point method of measurement in which the sample was alternately moved into and out of the beam, and could also be due to interference bands. The present data are less subject to these errors because the continuous method of recording data is more reliable and the large angular aperture of the Perkin-Elmer spectrometer reduces the chance of obtaining interference bands. The absence of fine structure was confirmed by measurements made with a large recording infrared spectrometer of much higher resolving power.*

The double reflection peak found by B–B–S in the region of 15 μ appears to be due to errors resulting from scattered light which are appreciable in the region of the CO_2 absorption band at 14·97 μ and in the wavelength region beyond 15 μ where the transmission of the NaCl prism is low.

As seen in the reflection curve, MgO is an excellent reflection filter for use with the KBr prism. However, since single crystals with large cross-sections are not readily available, it is necessary to place the filter at a focus point in the optical system.

DISCUSSION

According to the present data, the infrared properties of MgO do not differ in form from those of other sodium chloride-type crystals. Nevertheless definite differences become apparent when the absorption and reflection curves of the various NaCl-type crystals are compared with one another.

The absorption coefficient curves for MgO and for LiF and NaF (Hohls, 1937) in the short wavelength region of their absorption spectra are given in Fig. 6. Two well-defined secondary absorption peaks are found for MgO; only one peak is found for the other crystals. The absorption coefficients have the same order of magnitude, but the MgO peaks are more prominent and broader. The 11·82 μ peak in MgO also shows additional structure.

The reflection curves of MgO, and of LiF, NaF, NaCl and KCl for which accurate data are available (Hohls, 1937), are plotted on a logarithmic wavelength scale in Fig. 7. The major reflection peak is highest in MgO. The

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* The authors are indebted to Dr. D. C. Smith and Mr. R. A. Saunders of the Chemistry Division of the Naval Research Laboratory for making these measurements on their large prism spectrometer.

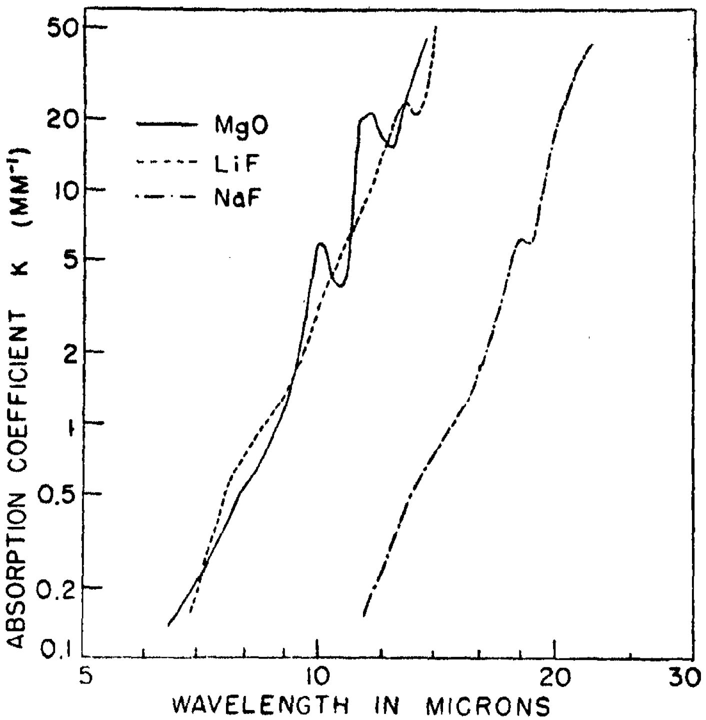

FIG. 6. Absorption coefficients of MgO and of LiF and NaF (Hohls, 1937).

$$k = -\frac{1}{d} \text{ en } \frac{1}{10}$$

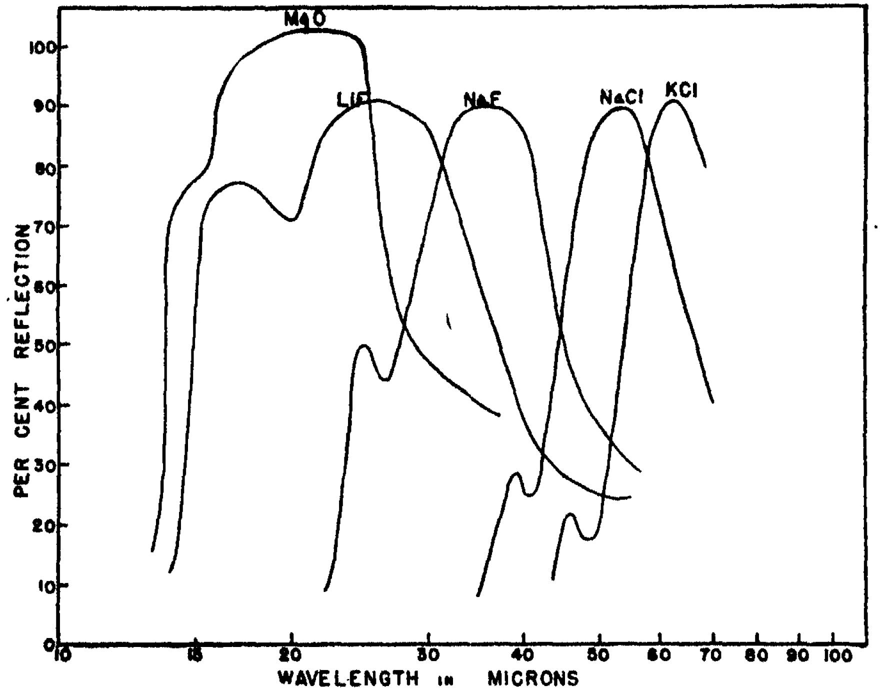

FIG. 7. Reflection of MgO and of some alkali halide crystals (Hohls, 1937) relative to an aluminum mirror.

fractional band width (width/peak wavelength) of the MgO major peak is probably smaller than that of LiF, but it is much larger than the values for the other alkali halides; the same relationship is present for the ratio of the heights of the minor and major peaks (minor peak/major peak). The values of these quantities given in Table I show that the fractional band widths and the height ratios decrease in the order LiF, MgO, NaF, NaCl and KCl. The two peaks are not separated in MgO as they are in the other crystals, so its values are less accurate than the others.

TABLE I

Crystal	Fructional Band Width	Height Ratio	Major Peak Wavelength μ	Minor Peak Wavelength μ
MgO ..	~·43	~·7	~22	~16
LiF ..	·46	·85	26	17
NaF ..	·34	·56	36	25
NaCl ..	·28	·32	53	39
KCl ..	·18	·25	63	46

Fractional band width = width of major peak in microns at 0·8 of peak height / wavelength of peak;

Height ratio = height of minor peak/height of major peak.

Without going into a detailed mechanism of infrared absorption, one can conclude from the broad reflection curve, the secondary bands in the absorption spectrum and the high auxiliary reflection peak of MgO that there is considerable coupling between the modes of vibration of its ions. This coupling is apparently more extensive in MgO and LiF than in the other crystals and decreases in the order NaF, NaCl and KCl.

A similar trend is found in these crystals for homopolar bonding and ion overlapping (Burstein and Smith, 1948 *b*). Therefore, it appears that the extent of coupling between modes of vibration can be correlated with these quantities. The relative amount of homopolar bonding in these crystals is shown in Table II by values of the strain polarizability λ_0 (change in molar polarizability with density) and the deviation of the elastic constants from the Cauchy relation. Data for NaF are not yet available.

Existing classical and quantum mechanical treatments of the coupling between the modes of vibration in crystals (Born and Blackman, 1933; Blackman, 1933; Barnes, Brattain, and Seitz, 1935; Raman, 1947) have attributed the secondary bands in the absorption spectra of ionic crystals to the anharmonic vibration terms (cubic and higher order terms in the potential function). These terms were introduced phenomenologically into

TABLE II

Crystal	λ_0	$\left\lvert \frac{C_{44}}{C_{12}} - 1 \right\rvert$	$\alpha \times 10^5$	θ °K.	$\sqrt{\mu^2}$ Å.
MgO ..	1·4	0·4	13	770	..
LiF ..	·7	0·3	34	..	..
NaF ..	..	..	36	440	·18
NaCl ..	·6	0·1	40	280	·24
KCl ..	·6	0·0	38	230	·26

λ_0 = strain polarizability (change in molar polarizability with density);
$\lvert C_{44}/C_{12} - 1 \rvert$ = deviation of the elastic constants from the Cauchy relation at room temperature;
α = linear temperature coefficient of expansion;
θ = Debye temperature;
$\sqrt{\mu^2}$ = root mean square of vibration amplitude of ions at 293° K. (Lonsdale, 1948).

the potential energy equation with arbitrary constants since there was no way to calculate them from fundamental considerations. Because of this, there have been no attempts to calculate the intensities and widths of the fundamental and secondary absorption bands from theory. At best it was only possible to show that the existence of secondary bands was not contradictory to the theory, and it was necessary to adjust constants in fitting the theory to the experiment.

According to these theories the coupling between vibrational modes is determined by the magnitude of the anharmonic vibration terms which can be estimated approximately from available data on the temperature coefficient of expansion. This coefficient is directly related to the amplitude of vibration of the ions and thus to the anharmonicity of the vibrations. Values for the coefficient of expansion, the root mean square amplitude of vibration of the ions, and also the Debye temperature for the crystals under consideration are given in Table II. The data shows that those crystals with the larger amount of coupling between vibrations are those with the smaller coefficients of expansion, smaller vibration amplitudes, and the higher Debye temperatures. One can conclude that the anharmonic terms contribute only slightly to the coupling between vibrations at room temperature.

It should be noted that the width of the reflection curves cannot be explained by temperature broadening alone since this broadening would be greater for those crystals with large vibration amplitudes and lower Debye temperatures. The width of the reflection curve is actually greater for the crystals with lower vibration amplitude and higher Debye temperature. The broad reflection peaks for MgO and LiF can only be attributed to the existence of a number of absorption bands, rather than to temperature broadening. Nevertheless, temperature broadening can partly explain the difference in character of the secondary bands found in the different crystals and the relatively large reflection peak observed in MgO. This is shown, for example, by the increase in height of the major reflection peak in LiF to 100 per cent. when the temperature is lowered to 87° K. (Korth, 1932).

Since the extent of coupling between the modes of vibration in ionic crystals can be correlated with the extent of homopolar bonding, the change in the polarizability with its accompanying change in the charge of the ions during vibration may be one of the important factors in the coupling mechanism (Burstein and Smith, 1948, *b*). That this is plausible can be readily seen from a consideration of the electric moment which determines the transition probabilities for the infrared-active vibrations.

The electric moment in a diatomic ionic crystal can be represented classically by an expression of the form

$$\mathrm{M} = qr,$$

where r is the instantaneous distance between the positive and negative ions and q is the instantaneous charge of the ions. In NaCl-type crystals where the vibrations are symmetrical, only quadratic changes in the polarizabilities manifest themselves. The periodic variations in the polarizabilities of the ions during vibration will, therefore, contain the frequency components $2\omega_1$, $2\omega_2$, $(\omega_1 \pm \omega_2), \ldots.$, where ω_1, ω_2, ..., are the frequencies of both active and inactive vibrations. Since the charge of the ions is related to the amount of homopolar bonding and consequently to the polarizability, the charge will also vary periodically at those frequencies.*

Assuming harmonic vibrations, the electric moment is given by an equation of the form

$$\mathrm{M} = q_0 \left[r_1 \sin \omega_1 t + r_2 \sin \omega_2 t + \ldots. \right] + r_0 \left[q_1 \sin 2\omega_1 t + q_{12} \sin (\omega_1 \pm \omega_2)\, t + q_2 \sin 2\omega_2 t \right]$$

where r_0, q_0 are the equilibrium distance and the corresponding charge of the ions; r_1, r_2, etc., are displacement amplitudes; and q_1, q_2, q_{12}, etc., are the charge amplitudes.

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* Owing to overlapping and homopolar bonding, there is some sharing of valence electrons and hence the average charge of the ions is not given simply by the valence. This has been demonstrated by calculations of electron distribution around the ions based on X-ray scattering data (Wollan, 1930). The change in charge with interatomic distance has also been used to explain the large dielectric constants of the heavy-metal halides (Eucken and Büchner, 1934).

Since the electric moment determines the transition probability and the intensity of absorption, the terms in the first bracket correspond to fundamental absorption bands due to active vibrations. The terms in the second bracket correspond to overtone bands, as well as sum and difference bands of both active and inactive vibrations. These are all included under secondary bands. A given vibration need not be infrared active in order to appear active in the sum and difference bands.

According to this equation the intensities of the secondary bands will depend on the magnitudes of the quadratic changes in the polarizability of the ions which take place during vibration. Data on the magnitude of these quantities is not available, but it seems reasonable to expect that crystals which exhibit relatively large changes in the average polarizability with change in average interatomic distance under homogeneous deformation will also have relatively large quadratic changes. An investigation of the intensities of the second-order Raman scattering of MgO and other NaCl-type crystals would yield the magnitude of these quantities more directly.

Although the electric moments and transition probabilities can be obtained more exactly from quantum mechanical considerations, the classical treatment employed here can be used qualitatively to describe the coupling mechanism. The major modification to the classical results introduced by quantum mechanics is the fact that the sum and difference bands have different intensities. The terms in the electric moment corresponding to the difference bands will contain a Boltzmann factor and will decrease rapidly in magnitude with decrease in temperature. This effect is analogous to that found for the intensities of the Stokes and anti-Stokes lines in Raman spectra. In addition, the vibration and charge amplitudes will be replaced by quantities which depend essentially on the differences of these amplitudes in the two states between which the transition is taking place. The effect of temperature on the summation bands will depend on the way these quantities change with temperature. The overlapping of the ions and the homopolar bonding increase as the temperature is decreased, so the overtone and summation terms in the electric moment and the corresponding absorption bands should persist even at low temperatures.

A similar equation for the electric moment can be written by including anharmonic vibrations and neglecting the change in charge of the ions. The two equations will be exactly alike in form. However, the physical interpretation of the terms involving the overtone and the sum and difference frequencies will be different. There is no way of distinguishing between the two equations from infrared data alone. This can only be done by correlating the infrared data with that obtained from other measurements.

After establishing the significance of the various terms in the equation, it should then be possible to estimate their magnitude and to make predictions concerning the relative intensities of the absorption bands in different crystals and their dependence on temperature. A complete theory will, of course, include anharmonic vibration terms which are especially important at higher temperatures.*

The suggestions concerning the role played by the strain polarizability in the coupling between vibrations do not depend on the particular mechanism of vibration which leads to infrared absorption. Additional information concerning the dynamic changes in polarizability with change in interatomic distance is needed before it will be possible to calculate exactly the intensities of the fundamental and secondary bands and their wavelengths. Nevertheless it should be possible to estimate the relative intensities of the absorption bands and to predict the effect of temperature. These aspects of the problem will be treated in a later paper which will also give a more detailed discussion of the concepts which have only been qualitatively presented here.

The authors wish to acknowledge Sir C. V. Raman's stimulating interest in this investigation and the valuable discussions they have had with him.

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* M. Born (1945) has recently suggested that the secondary bands can be explained quantum mechanically by second-order terms in the electric moment and that anharmonic vibration is not needed.

SPECTRES DE RAMAN DU CHLORURE ET DU BROMURE D'AMMONIUM

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1. INTRODUCTION

LE chlorure, le bromure et l'iodure d'ammonium se présentent sous plusieurs formes cristallines, dont les domaines d'existence sont séparés par des températures de transition. On a étudié de nombreuses propriétés physiques de ces composés: dilatation,[1] chaleur spécifique,[2] constante diélectrique,[3] piézoélectricité,[4] réfringence,[4] diffraction des rayons X;[5] et des électrons,[6] spectre d'absorption infrarouge,[7] et spectre de Raman.[8]

L'ensemble des propriétés de ces cristaux n'est pas encore expliqué de façon entièrement satisfaisante par les structures que l'on a pu imaginer pour eux. En particulier, une des questions qui demeurent les plus incertaines est celle de la symétrie et des degrés de liberté que l'on doit attribuer aux ions NH_4^+. Il nous a paru que la théorie de la polarisation des raies de Raman dans les cristaux cubiques, que nous avons développée récemment,[9] pourrait aider à aborder le problème précédent. Aussi, avons nous entrepris des recherches sur le spectre de Raman de monocristaux de chlorure, de bromure et d'iodure d'ammonium. Nous indiquerons et discuterons seulement ici les résultats relatifs aux spectres de ces deux premiers composés, à la température ordinaire.

Rappelons d'abord brièvement que les oscillations fondamentales d'un cristal cubique actives dans l'effet Raman se divisent en trois types, d'après leur symétrie par rapport aux axes ternaires et binaires du groupe du tétraèdre (la considération des éléments de symétrie des autres groupes du système cubique ne modifie pas ce classement). On distingue: les oscillations A, simples et totalement symétriques; les oscillations E, doublement dégénérées par rapport aux axes ternaires; les oscillations F, triplement dégénérées. Pour les vibrations simples, le facteur de dépolarisation ρ est toujours égal à 0, quelle que soit l'orientation du cristal; mais ρ varie, selon les cas, pour les vibrations doubles entre 0 et 3; pour les vibrations triples, entre ½ et 2.

2. RESULTATS EXPERIMENTAUX

Le tableau I contient les résultats des mesures faites à 20°-25° C, exprimés au moyen des notations suivantes. Pour les intensités, I indique une raie forte, *m* une raie moyenne, *f* une raie faible. Pour l'aspect, *s* désigne une raie fine, *d* une raie diffuse, *b* une bande.

TABLEAU I

Chlorure d'ammonium				Bromure d'ammonium			
$\Delta\nu$ en cm.$^{-1}$	Type	Intensité	Aspect	$\Delta\nu$ en cm.$^{-1}$	Type	Intensité	Aspect
88	E	6, 3	*d*	56	E	I	*s*
				130	?	*m*	*d*
143	F	10	*d*	136	F	I	*d*
170	F	9, 5	*d*	147	F	I	*d*
197	F	..	*d*	172-182-209	?	*m*	*b*
				1370	?	*tf*	*s*
1403	F	3, 8	*s*	1400	F	I	*s*
1428	F	0, 7	*s*	1422	F	*f*	*d*
1444	F	0, 4	*s*	1687	E	TI	*s*
1711	E	9, 0	*s*	1710	F	*m*	*d*
1771	F	3, 3	*b*	1955	F	I	*b*
1995	F	3, 5	*b*	2804	F	I	*d*
2818	F	12	*d*	3035	F	TI	*d*
3042	A(+F)	51	*d*	3055	A	TI	*d*
3133	F	20	*d*	3126	F	TI	*d* (doublet?)
				3282-3318	F	*m*	*b*

De plus le spectre du bromure d'ammonium contient un certain nombre de raies très faibles dont nous n'avons pas pu déterminer le type et dont nous indiquons seulement la fréquence et l'aspect.

TABLEAU II

$\Delta\nu$ en cm.$^{-1}$	258	312	345-472	596-680	997	1016	1032	1071-1130	1160
Aspect ..	*d*	*d*	*b*	*b*	*s*	*s*	*s*	*b*	*s*

3. DISCUSSION DES RÉSULTATS

L'analyse des cristaux par les rayons X[5] montre avec certitude qu'à la température ordinaire les atomes N et Cl (ou Br) sont disposés comme les atomes Cs et Cl dans les cristaux subiques de chlorure de césium (groupe O_h^1—Pm 3m, symétrie propre de N et de Cl ou de Br : O_h-4/m $\bar{3}$ 2/m ; Z = 1). Mais l'étude aux rayons X ne permet pas de déterminer la place des quatre atomes H qui entourent chaque atome N.

Spectre de basse fréquence.—Nous discuterons d'abord les relations qui existent entre la symétrie possible des ions NH_4^+ et le spectre de Raman de basse fréquence que l'on prévoit en considérant ces ions comme rigides et susceptibles d'effectuer des déplacements. Ceux-ci donnent naissance soit à des oscillations de translation, soit à des oscillations de rotation ou librations.

Dans tout ce qui suit nous admettrons que tous les ions NH_4^+ du cristal ne forment qu'une famille, au point de vue de la symétrie. On parviendrait à plus de possibilités que nous n'en considérerons, en renonçant à cette supposition; mais nous verrons que l'on peut la justifier, en étudiant les spectres de haute fréquence.

L'hypothèse la plus simple consiste à supposer que les ions NH_4^+ ont la forme de tétraèdres réguliers et une orientation bien déterminée. Leur symétrie propre est alors celle du goupe T_d; elle est compatible avec l'holoédrie du cristal (groupe O_h^5), en admettant que la maille est double, ou avec son hémiédrie (groupe T_d^1). Ces deux possibilités correspondent respectivement aux dispositions désignées sous le nom de " antiparallèle " et "parallèle" par Menzies et Mills.[10] Aucune libration des ions NH_4^+ n'est active dans ce cas, car leur ellipsoïde de polarisabilité est une sphère.

On peut également supposer que les ions NH_4^+ n'ont pas une forme tétraédrique régulière et que l'un des atomes H se distingue par la formation d'une liaison particulièrement forte avec l'atome d'halogène. Cette hypothèse qui est compatible avec les propriétés chimiques des halogénures d'ammonium, conduit à attribuer à l'ion NH_4^+ la symétrie C_{3v} ou C_3, selon l'orientation occupée par les trois atomes d'hydrogène identiques autour de l'axe privilégié N-H-Cl. Pour trouver la symétrie cubique du cristal, il faut alors admettre que la maille est multiple et contient Z ions NH_4^+. Selon que les axes ternaires des divers ions sont parallèles ou antiparallèles, la symètrie C_{3v} correspond pour l'ensemble du cristal au groupe T_d^3 $(Z = 4)$ ou O_h^1 $(Z = 8)$, la symétrie C_3 au groupe T_d^4 $(Z = 8)$ ou bien à l'un des groupes O^1 $(Z = 8)$, T_h^1 ou T_h^9 $(Z = 8)$. Dans tous ces cas, les librations desions autour d'axes perpendiculaires à l'axe ternaire sont seules actives, car l'éllipsoïde de réfractivité est de révolution.

Mais l'existence d'ions NH_4^+ occupant des positions moyennes fixes, autour desquelles ils effectuent des vibrations ou des librations, à la température ordinaire, a été mise en doute par Pauling,[11] qui a supposé que la température de transformation correspond au passage des librations à la rotation libre des ions. Cette conception conduit à attribuer aux ions NH_4^+ une symétrie propre qui dépend de la manière dont on conçoit cette rotation. Dans l'idée de Pauling, il s'agit d'une rotation autour d'axes quelconques, donc isotrope en moyenne; cela entraine pour les ions NH_4^+, considérés comme un tout, soit la symétrie O_h et pour le cristal le groupe O_h^1; soit la symétrie O et pour le cristal les groupes O^3 (Z = 1) ou O_h^6 (Z = 2).

L'hypothèse de la rotation libre a été critiquée par Frenkel,[18] qui la remplace par la conception suivante: les molécules ou les ions effectueraient des librations au-dessus du point de transition comme au-dessous; mais tandis qu' àbasse température les librations se feraient autour d'axes d'orientation bien définie dans la maille, à température élevée elles se produiraient autour d'axes orientés au hasard, comme dans un liquide. Dans ce cas, les calculs relatifs aux raies de libration devraient être conduits comme dans un liquide; leur facteur de dépolarisation devrait avoir une valeur égale à 6/7, quelle que soit l'orientation du cristal, ce qui est en contradiction avec les faits expérimentaux.

Toutefois, la rotation des ions NH_4^+ ne peut pas être nécessairement isotrope. Pour interpréter les variations thermiques de la constante diélectrique des halogénures d'ammonium, Bauer[3] a fait l'hypothèse d'une rotation des ions NH_4^+ autour d'un de leurs axes ternaires, c'est-à-dire de la direction d'une des liaisons N–H. Cette direction est ainsi privilégiée et l'on retrouve pour l'ion la symétrie C_{3v} ou C_3 discutée plus haut au point de vue statique.

Le tableau III rassemble les diverses possibilités envisagées pour la symétrie des ions NH_4^+ et des cristaux de chlorure et de bromure d'ammonium, ainsi que le dénombrement des raies de Raman de basse fréquence qui peuvent provenir des oscillations fondamentales de translation ou des librations; ces dernières ne se manifestent que si les ions NH_4^+ ne sont pas en rotation isotrope.

TABLEAU III

Symétrie de NH_4^+	Symétrie du cristal	Z	Translations	Librations
O_h ..	O_h^1	1	0	0
O ..	O^3	1	$1F_2$	0
	O_h^6	2	$1F_{2g}$	0
T_d ..	T_d^1	1	$1F_2$	0
	O_h^5	2	$1F_{2g}$	0
C_{3v} ..	T_d^2	4	$1A_1$, 1E, $4F_2$	1E, $1F_2$
	O_h^1	8	$1A_{1g}$, $1E_g$, $2F_{2g}$	$1E_g$, $1F_{2g}$
C_{3u} ..	O^1	8	$1A_1$, 2E, $4F_2$	2E, $2F_2$
	T_d^4	8	$1A_1$, 2E, $6F_2$	2E, $2F_2$
	T_h^1 o T_h^6	8	$1A_g$, $1E_g$, $3F_g$	$1E_g$, $2F_g$

Cela posé, la comparaison des prévisions contenues dans le tableau III avec les résultats expérimentaux montre que l'hypothèse d'une symétrie C_{3v} ou C_3 pour les ions NH_4^+ est seule compatible avec le nombre des raies de basse fréquence contenu dans le spectre de Raman, sans que ce nombre ou le type des raies permette de faire un choix plus précis entre les divers groupes possibles pour le cristal. Mais on peut invoquer des arguments tirés de l'étude d'autres phénomènes.

La disparition de la piézoélectricité du chlorure d'ammonium au dessus de —30°[4] et son absence dans le bromure sont peu compatibles avec l'un des groupes de symétrie T, O ou T_d pour le cristal.

La recherche du pouvoir rotatoire nous a montré que la rotation n'atteint pas 1' par mm pour le chlorure et 0, 1' par mm pour le bromure, dans les échantillons que nous avons examinés; ce résultat rend improbable que les cristaux appartiennent à l'un des groupes T ou O. Enfin les figures de corrosion par l'eau, que nous avons faites sur le chlorure, ne révèlent aucune hémiédrie.

Cet ensemble de raisons laisse à penser que les cristaux de chlorure et de bromure d'ammonium appartiennent vraisemblablement au groupe holoèdre du système cubique, à la température ordinaire. Ce serait donc pour le cristal la symétrie O_h (ou T_h) et pour les ions NH_4^+ la symétrie C_{3v} (ou C_3) qui seraient les plus vraisemblables.

Lawson[3] a indiqué que les mesures de la chaleur spécifique C_v du chlorure d'ammonium au voisinage du point de transition demande une contribution de 6 cal. mol/degré pour les mouvements des ions NH_4^+, et il a signalé que ce résultat s'accorde avec l'hypothèse de Frenkel, mais non avec celle de Pauling, qui n'en donne que trois. L'hypothèse de Bauer fournit 5 cal. mol/degré, ce qui est beaucoup plus proche du résultat de Lawson.

Spectre de haute fréquence.—Il doit être dû essentiellement au oscillations internes des ions NH_4^+. On sait que le spectre de Raman des halogénures d'ammonium en solution contient quatre raies, ce qui correspond bien aux quatre fréquences fondamentales actives d'un édifice pentatomique en forme de tétraèdre régulier. Par suite, en attribuant la symétrie T_d à l' ion NH_4^+ contenu dans la maille d'un cristal du groupe O_h^5, on ne parviendra pas à rendre compte du grand nombre de raies qui apparaissent au dessus de 1000 cm^{-1} dans le spectre du chlorure et du bromure d'ammonium.

D'autre part, la symétrie O_h ou O des ions NH_4^+ ne se conçoit que statistiquement, dans l'hypothèse d'une rotation libre autour d'axes pouvant prendre avec une égale probabilité toutes les orientations possibles. Or dans ce cas, le facteur de dépolarisation devrait avoir la même valeur que celui des raies de l'ion en solution, soit O ou 6/7 selon le type d'oscillation, au lieu des valeurs calculées pour un cristal cubique[9] et variables avec l'orientation. Ce résultat est en contradiction avec les résultats de nos mesures. Pour la même raison, l'hypothèse de Frenkel ne s'accorde pas avec les faits, pour le spectre de haute fréquence comme pour celui de basse fréquence.

Reste à examiner les conséquences de la symétrie C_{3v} ou C_3 pour les ions NH_4^+. C'est le couplage des oscillations fondamentales des ions contenus dans la maille qui fournit le nombre et les types des raies du spectre.[9] Ce couplage se fait sans difficultés si l'on admet que les ions occupent des positions moyennes bien définies; si, au contraire, ils tournent autour de leur axe ternaire, la définition du couplage devient plus délicate; elle conduit au même résultat que dans la première hypothèse, seulement lorsque les rotations des ions ont lieu d'une façon totalement symétrique et que l'on néglige l'interaction de la rotation et de la vibration. Il est possible de faire bien d'autres hypothèses: nous ne les développerons pas ici. Dans ces conditions, on parvient au tableau suivant, que permet de comparer les prévisions théoriques aux données de l'expérience. Nous y avons fait figurer les raies les plus intenses en caractères italiques.

TABLEAU IV

<table>
<tr><td rowspan="9">Théorie</td><td rowspan="3">Ion NH_4^+ T_d</td><td>Vibr.</td><td colspan="2">ν_4</td><td>ν_2</td><td>ν_1</td><td colspan="2">ν_3</td></tr>
<tr><td>$\Delta\nu$</td><td colspan="2">1397</td><td>1685</td><td>3033</td><td colspan="2">3134</td></tr>
<tr><td>Type</td><td colspan="2">F</td><td>E</td><td>A</td><td colspan="2">F</td></tr>
<tr><td colspan="2">Ion $NH_4^+C_{3v}$</td><td>A_1</td><td>E</td><td>E</td><td>A_1</td><td>A_1</td><td>E</td></tr>
<tr><td rowspan="2">Cristal</td><td>T_d^3</td><td>A_1 F_2</td><td>E F_2</td><td>E F_2</td><td>A_1 F_2</td><td>A_1 F_2</td><td>E F_2</td></tr>
<tr><td>O_h^1</td><td>A_{1g} F_{2g}</td><td>E_g F_{2g}</td><td>E_g F_{2g}</td><td>A_{1g} F_{2g}</td><td>A_{1g} F_{2g}</td><td>E_g F_{2g}</td></tr>
<tr><td colspan="2">Ion $NH_4^+C_3$</td><td>A_1</td><td>E</td><td>E</td><td>A_1</td><td>A_1</td><td>E</td></tr>
<tr><td rowspan="2">Cristal</td><td>O^1 ou T_d^4</td><td>A_1 F_2</td><td>2E $2F_2$</td><td>2E $2F_2$</td><td>A_1 F_2</td><td>A_1 F_2</td><td>2E $2F_2$</td></tr>
<tr><td>T_h^1 ou T_h^6</td><td>A_g F_g</td><td>E_g $2F_g$</td><td>E_g $2F_g$</td><td>A_g F_g</td><td>A_g F_g</td><td>E_g $2F_g$</td></tr>
<tr><td rowspan="4">Expérience</td><td rowspan="2">$ClNH_4$</td><td>$\Delta\nu$</td><td colspan="2">*1403* 1428 1444</td><td>*1711* 1771 1995</td><td>*3042*</td><td>*2818*</td><td>*3188*</td></tr>
<tr><td>Types</td><td colspan="2">F F F</td><td>E F F</td><td>A(+F)</td><td>F</td><td>F</td></tr>
<tr><td rowspan="2">$BrNH_4$</td><td>$\Delta\nu$</td><td colspan="2">1370 *1400* 1422</td><td>*1687* 1710 1955</td><td>*3035* *3055*</td><td>*2804*</td><td>*3126*</td></tr>
<tr><td>Types</td><td colspan="2">F F F</td><td>E F F</td><td>F A</td><td>F</td><td>F</td></tr>
</table>

On voit aussitôt que le nombre des raies observées ne s'accorde ni avec la symétrie T_d de l'ion NH_4^+ (on s'attendrait à trouver quatre raies fines), ni avec l'hypothèse de Pauling ou celle de Frenkel, qui laissent prévoir quatre raies floues, dont trois polarisées à 6/7.

L'oscillation totalement symétrique ν_1 de l'ion NH_4^+ doit donner naissance, dans toutes les hypothèses envisagées, à une raie de type A et une de type F. Dans le chlorure, l'étude de la polarisation de la raie 3042 cm.$^{-1}$ montre qu'elle est formée de deux composantes; celles-ci se séparent nettement dans le bromure en 3035 et 3055 cm.$^{-1}$, qui ont les types prévus. En l'absence de mesures de polarisation, Krishnan[8] n'a pu les distinguer à la température ordinaire; il trouve bien deux raies (3037 et 3078 cm.$^{-1}$) á 173° K, mais l'explication de l'origine de ce doublet par une résonance de Fermi est inacceptable, puisque les deux raies n'ont pas le même type. La raie F (3035 cm.$^{-1}$) devrait avoir une intensité nulle si l'ion NH_4^+ gardait dans le cristal la symétrie T_d; or, elle apparait nettement dans le spectre du chlorure et fortement dans celui du bromure: c'est là une preuve très nette de l'abaissement de symétrie de l'ion NH_4^+.

Si l'attribution que nous avons faite est correcte, en plaçant les bandes 1995 (chlorure) et 1955 (bromure) dans l'ensemble des oscillations dérivées de la fréquence ν_2 de l'ion libre, les résultats expérimentaux semblent s'accorder mieux avec la symétrie T_h du cristal qu'avec la symétrie O_h; mais on ne peut considérer cette preuve comme décisive.

Il est peu probable que les raies 2818 cm.$^{-1}$ (chlorure) ou 2804 cm.$^{-1}$ (bromure), plus fortes que les raies 1403 cm.$^{-1}$ ou 1400 cm.$^{-1}$ des mêmes spectres, soient les harmoniques de ces raies. Nous les avons classées dans l'ensemble ν_3. En supposant, en effet, que la cessation de dégénérescence de ν_3 provienne de la diminution de la force d'une liaison N–H, on peut montrer, en adoptant le système des forces de valence[13] que la fréquence de l'une des deux oscillations dérivées dans un ion ne change pas et que celle de l'autre doit diminuer.

L'aspect des raies du spectre de haute fréquence varie beaucoup de l'une à l'autre. Les raies de type E dérivées de l'oscillation ν_2 sont fortes et fines; le fait qu'elles sont toujours uniques est en faveur de l'existence d'une seule famille d'ions NH_4^+ dans les cristaux étudiés. Les raies correspondant aux oscillations de valence ν_1 et ν_3 sont toutes diffuses, même la raie totalement symétrique bien isolée 3055; cela semble indiquer une variation au cours du temps du champ qui entoure l'ion.

Dans aucun cas, nous n'avons aperçu de structure fine des raies d'oscillation internes. Une telle structure a été mise en évidence par Beck[7] pour les bandes d'absorption infrarouges correspondant à la fréquence ν_2; si elle est réelle, on peut encore se demander si elle correspond à une structure de rotation ou à des bandes de combinaison vibration + librations.

Remarquons que la concordance excellente entre les fréquences des raies de Raman et des bandes d'absorption infrarouges relatives aux oscillations internes[7] est en faveur de la symétrie C_{3v} ou C_s des ions NH_4^+, ces deux groupes finis étant les seuls dont les oscillations fondamentales soient actives à la fois en absorption et en diffusion.

4. CONCLUSIONS

L'étude de la polarisation du spectre de Raman des monocristaux cubiques de chlorure et de bromure d'ammonium, dans diverses orientations, permet d'attribuer les principales raies de ces spectres à des types d'oscillations bien déterminés.

L'interprétation du spectre de basse fréquence se fait de façon satisfaisante sans invoquer les oscillations du second ordre. Elle conduit, de même que l'étude du spectre de Raman de haute fréquence et la comparaison avec le spectre infrarouge, à écarter la forme tétraédrique régulière pour les ions NH_4^+, ainsi que les conceptions de Pauling et de Frenkel sur l'état de mouvement de ces ions au-dessus de la température de transition.

L'ensemble des résultats expérimentaux conduit à adopter une maille cristalline multiple, et rend probable la symétrie O_h ou T_h pour les cristaux, C_{3v} ou C_s pour les ions NH_4.$^+$ Ce dernier résultat peut s'accorder avec une rotation ou une libration anisotrope des ions NH_4.$^+$

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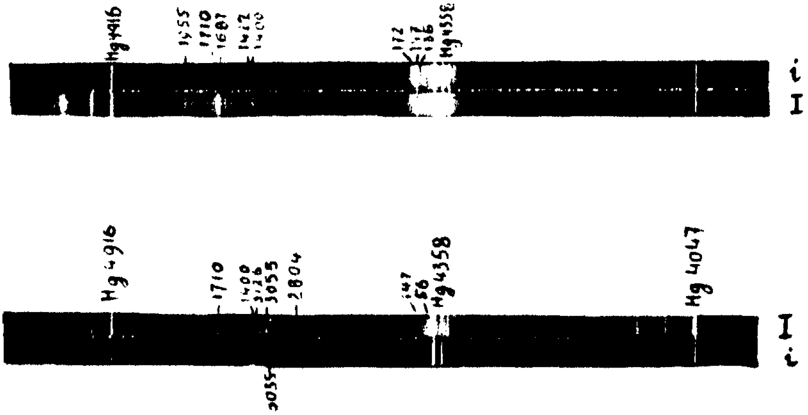

Bromure d'ammonium orienté selon les faces du cube

THE INFLUENCE OF OPTICAL ACTIVITY ON LIGHT-SCATTERING IN QUARTZ

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1. INTRODUCTION

IN a previous paper, the present writer (1947) has shown how the large rotatory power of quartz in the ultraviolet manifests itself in transverse light-scattering. A plane-polarised beam of intense λ 2537 radiation of a water-cooled magnet-controlled mercury arc traverses a perfectly clear and transparent sphere of quartz along the optic axis. A photograph of its track taken in a direction transverse to it exhibits marked fluctuations in intensity along its length. The effect is obviously due to the incident light vector being alternately parallel and perpendicular to the direction of observation and to the strong polarisation of genuine thermal scattering. In a similar effect observed earlier by Lord Rayleigh (1919) in smoky quartz, the strong Tyndall scattering of visible light by the inclusions present was utilised.

In the present investigation, the light scattered by transparent quartz is analysed spectroscopically and the banding for the individual Rayleigh and the more intense Raman lines recorded separately. Also by the use of a mercury vapour filter placed in the path of the scattered light, the Tyndall scattering of λ 2537 radiation due to inclusions in the crystal is suppressed efficiently and the genuine Brillouin components are recorded. The obliteration of the bands when the incident light traverses a sphere of clear quartz at small angles to the optic axis is also recorded and an explanation given.

2. EXPERIMENTAL TECHNIQUE

A transparent and practically colourless regular hexagonal crystal of quartz 4 cm. long, kindly lent by Prof. R. S. Krishnan, is employed for the purpose of the experiment. Two ends of it are cut normal to the optic axis. These ends and the sides are all ground and polished. As the crystal contained a few visible inclusions, the best portion is chosen.

The crystal is mounted with its optic axis vertical and one of the hexagonal sides facing the spectrograph. A sealed Z-type horizontal quartz mercury arc is water-cooled and magnet-controlled to give intense λ 2537 radiation. A rectangular aperture of 1 cm. × 0·5 cm. in front of the arc limits the beam. The light from it is condensed by a quartz lens of focal length 9 cm. for λ 2537 and aperture 4 cm. on one of the end surfaces of the crystal so that the beam traverses vertically along the optic axis. A large double-image prism next to the quartz lens served to polarise the beam, one of the images being screened off at the surface of the crystal. The vertical track of the beam in the crystal is focussed on the slit of a Hilger intermediate quartz spectrograph by a quartz lens. As the lens is not achromatic, its position is adjusted to give the best focus for λ 2537 radiation. With a slit width of 0·14 mm., the spectrum is photographed on a Selochrome plate giving an exposure of the order of 50 hours. A mercury vapour filter is employed in the path of the scattered light to absorb efficiently the Tyndall scattering of λ 2537 radiation and thus, record only the Brillouin components due to it.

3. Results and Discussion

A reproduction from the previous paper is given in Fig. 1 *b*, Plate VII, for comparison and shows clearly the bands in a perfectly clear and transparent sphere of quartz traversed by intense λ 2537 radiation. Owing to its high intrinsic intensity and the operation of λ^{-4} law, only the scattering of λ 2537 radiation is recorded even though no filter is employed in the incident light. Both its Rayleigh and Raman scattering would contribute to the intensity and as is well known, in a clear specimen of quartz, the latter makes as much as one fourth the contribution (Landsberg, 1927; Bhagavantam and Venkateswarulu, 1944). The pictures taken in the present investigation using a spectrograph are reproduced in Figs. 1 (*b*) and 1 (*c*). The complete spectrum [see Fig. 1 (*c*)] shows clearly the variation in the band width for different mercury arc lines. A major portion of their intensity recorded on the plate has its origin in the Tyndall scattering by the few inclusions present in the crystal. This is supported by the non-appearance of the intense 466 cm.$^{-1}$ Raman line (the absolute intensity of which is about 1/5 the intensity of the genuine Rayleigh scattering) excited by any mercury line other than λ 2537. On the other hand, as the λ 2537 radiation has been completely suppressed by the mercury vapour filter, what is observed in its place is the banding due to the Brillouin components arising from thermal scattering.

Fig. 1 (*a*) is a high enlargement of the portion between λ 2537 and the triplet λ 2654. It shows clearly the bands for the Brillouin components of λ 2537 and the two symmetric Raman lines 207 and 466 cm.$^{-1}$ excited by it, while the strong line 128 cm.$^{-1}$ and the weaker 800 (doublet) and 1159 cm.$^{-1}$ lines belonging to the degenerate class E, sub-groups E_1, E_2 and E_3 respectively, show no trace of the banding. It is clear from the work of Saxena (1940) and more recently of Krishnan (1945) that the Raman spectrum of quartz consists in the main of 12 first order lines including two doublets. Of these four lines 207, 357, 466 and 1082 cm.$^{-1}$ lines belong to the symmetric class A which are always completely polarised and should, therefore, show the bands. The rest belong to the degenerate class E divided into three sub-groups depending on their depolarisation values and orientation effects. However, in all sub-groups, as a result of degeneracy the two directions perpendicular to the optic axis are equivalent. This has an important consequence that when light is incident along the optic axis, the scattered intensity would be the same whether the light vector is along or perpendicular to the direction of observation (*vide* Table V of p. 109 of Saxena's paper). This prediction has been beautifully confirmed in the case of quartz for the first time in the present work; the more intense degenerate lines 128, 800 (doublet) and 1159 cm.$^{-1}$ lines showing no trace of the banding. The large optical activity of quartz along the optic axis has been a disturbing factor when it is required to study the effect of polarising an incident beam travelling along that direction. Hence, for such directions, studies have been confined till now to the use of incident unpolarised light. The present arrangement described enables one to make polarisation and intensity measurements using polarised light traversing along the optic axis, and the disturbing factor, namely the optical activity itself is made use of for the purpose. It is interesting to note that some of the degenerate lines, *e.g.*, 800 cm.$^{-1}$ line (E_2 sub-group) and 1159 cm.$^{-1}$ line (E_3 sub-group), have depolarisation values of ∞ and 0 respectively and still show no banding as expected.

The band width for λ 2537 and for the two 207 and 466 cm.$^{-1}$ Raman lines was measured with a glass scale reading to tenths of a millimetre and the reduction produced by the condensing lens and by the spectrograph for λ 2537 along the length of the slit was determined. From this, the actual width, which corresponds to a rotation of 180° of the plane of polarisation of the incident light, was calculated and hence, the rotation per millimetre for λ 2537 deduced. The calculated rotation of 148°·5 per mm. agrees well with the correct value of 148°·6 per mm. It is particularly interesting to note that the band widths of the Raman lines and the exciting line are identical [see Fig. 1 (*a*)]. A Rayleigh line of the same frequency as the 466 cm.$^{-1}$ line excited by λ 2537 would have shown about $\frac{1}{6}$ of a band less in 7 bands and this would have been shown up clearly.

4. DIRECTIONS INCLINED TO THE OPTIC AXIS

As a plane-polarised light beam advances inside a birefringent solid, it undergoes a periodic cycle of changes in its state of polarisation. Hence, its track made visible by the scattered light would exhibit striking fluctuations in intensity along its length. These bright and dark bands have been observed and photographed by the author (1947) using synthetic organic glasses with permanent strains and hence, behaving like very feebly birefringent solids. Now it follows that in a solid showing both optical activity and birefringence, the effect should also be observable. As is well known, quartz has both optical activity and birefringence for directions inclined to the optic axis.

For such directions, the theory of propagation of light in quartz has been dealt with by several workers (Briot, 1863; Gouy, 1885 and Wiener; *vide* Pockel, 1906). Along such directions, two similar elliptically polarised waves but with opposite sense of rotation and lying crossed to each other (*i.e.*, the major axis of one falls on the minor axis of the other) travel unchanged. The axes of the ellipses coincide with the principal planes. Pockels has shown in his book a simple though approximate way of arriving at the ratio of the axes of the vibration ellipses which propagate unchanged and the path difference between the two waves per unit length. If ρ is the rotatory power per unit length along any direction and δ_0 is the path difference due to birefringence alone (if $\rho = 0$), then the actual path difference per unit path between the two elliptic waves is given by

$$\delta = \sqrt{\delta_0^2 + (2\rho)^2}$$

and the ratio of the axis χ is given by

$$\chi = \tan\beta \text{ where } \tan\beta = \frac{2\rho}{\delta_0}$$

or

$$\chi^2 = \frac{\delta - \delta_0}{\delta + \delta_0}.$$

Bruhat (1935) has determined recently the rotatory power of quartz for directions parallel and perpendicular to the optic axis for different wavelengths.

For $\lambda\,2537$ $r_1 = -86°$ per mm. perpendicular to the optic axis

$r_3 = 149°$ per mm. parallel to the optic axis

$$\rho = r_1 \sin^2\phi + r_3 \cos^2\phi$$

where ϕ is the inclination of the ray with the optic axis. The two refractive indices for $\lambda\,2537$ are

$$n_\epsilon = 1{\cdot}60930, \qquad n_\omega = 1{\cdot}59830$$

For different values of ϕ the rotation and the path retardation per unit length are given in Table I.

TABLE I

ϕ in degrees	ρ' in degrees/mm.	ρ/π per mm.	$\delta_0/2\pi$ per mm.	$\delta/2\pi$ per mm.	$2\pi/\delta$ in mms.	χ
0	149·0	0·8278	0	0·8278	1·208	1
1	148·93	0·8276	0·01315	0·8277	1·208	0·9784
2	148·7	0·8264	0·05229	0·8281	1·208	0·9387
3	148·4	0·8244	0·1174	0·8327	1·201	0·8677
4	147·9	0·8218	0·2091	0·8480	1·179	0·7774
5	147·2	0·8177	0·3264	0·8804	1·135	0·6775
6	146·4	0·8130	0·4687	0·9383	1·066	0·5778
7	145·5	0·8084	0·6377	1·0296	0·9716	0·4848
7·86	144·6	0·8032	0·8032	1·1359	0·8805	0·4142
8	144·4	0·8019	0·8318	1·1554	0·8655	0·4035
9	143·2	0·7954	1·049	1·3165	0·7498	0·3363
10	141·9	0·7885	1·294	1·5153	0·6601	0·2806
11	140·5	0·7806	1·562	1·7462	0·5726	0·2360
12	138·8	0·7706	1·855	2·0172	0·4958	0·2043
13	137·1	0·7617	2·172	2·3045	0·4340	0·1713
14	135·2	0·7513	2·512	2·6219	0·3814	0·1463
15	133·3	0·7407	2·874	2·9679	0·3369	0·1268
20	131·5	0·6752	5·020	5·0652	0·1974	0·0670
30	90·2	0·5009	10·73	10·7417	0·0931	0·0233
52·69	0	0	27·22	27·22	0·0367	0
90	−86	0·4778	43·37	43·3726	0·0231	0·0055

$2\pi/\delta$ for any value of ϕ gives the periodic distance after which the incident polarised beam proceeding along that direction returns to its original state of polarisation after undergoing a cycle of changes. It is seen, however, from the table that this length changes but little up to 3°. Hence, when light goes along the optic axis convergence angles of the order of 6° can be used, and the bands in transverse light-scattering would still be clear. On the other hand, at say 8° to the optic axis, when the periodic length is appreciably different, it changes so rapidly with the angle that unless the beam is strictly parallel, the rays going at different angles obliterate the banding. These conclusions have been verified in the observations made with the sphere of quartz. The arrangement used has already been described in the earlier paper.

Fig. (2), Plate VII, shows the bands clearly when a fairly wide beam travels exactly along the optic axis. At 4° to the optic axis the bands are still clear and of the same width and are reproduced in Fig. 2 (*b*). At the edge of the track away from the optic axis the banding is just obliterated. At 8° to the optic axis the series of pictures, Figs. 2 (*c*), (*d*) and (*e*) show the effect of narrowing the beam. With a wide beam [Fig. 2 (*c*)] some rays are going very near the optic axis and hence, show the banding while on the other side the bands are obliterated. When the beam is strictly limited, the bands have been completely obliterated. At 10° [Fig. 2 (*e*)] the bands have disappeared even with a fairly wide beam. The maximum convergence of the incident light used is about 8° to 10° while the minimum used is about 2°.

It should be recalled that in a purely optically active solid the banding would be equally clear in any azimuth transverse to the beam. On the other hand, in a birefringent solid without optical activity, the banding would be marked only when both the direction of the incident light vector and that of observation are inclined at 45° to the principal planes. When either direction coincides with the principal plane the banding would disappear. Hence, for directions away from the optic axis, the sphere of quartz is rotated so that the bands would be most marked and yet the banding vanished at 10°. The value of χ in the last column of Table I gives a measure of the azimuth effect if strictly parallel light is used.

It is interesting to note that in the visible say at λ 4358, the ratio of the rotatory power to birefringence of quartz is half that for the ultra-violet λ 2537. Hence, to get equal clarity of the banding, the square of the convergence angles used should be only half as large in the visible compared to the ultra-violet. This result has also been verified (no photograph is reproduced).

In the previous paper, it was reported that the sphere of quartz used was a left-handed one. Between crossed polaroids, the observation recorded that the rings of any particular colour appear to expand indicates actually that the sphere is a right-handed one (Cady, 1946).

In conclusion, the author wishes to thank Prof. Sir C. V. Raman and Prof. R. S. Krishnan for their keen interest in the work and for the useful discussions he had with them.

5. SUMMARY

A vertical plane-polarised beam of intense λ 2537 mercury radiation travels along the optic axis of a crystal of quartz and the light vector is alternately parallel and perpendicular to the direction of observation transverse to the beam. A spectral analysis of the scattered light, using a mercury vapour filter to absorb the λ 2537 line, yields bands of fluctuating intensity along the length of the slit for the Brillouin components and for the two symmetric 207 and 466 cm.$^{-1}$ Raman lines. On the other hand, the degenerate lines 128,800 (doublet) and 1159 cm.$^{-1}$ lines belonging to the different

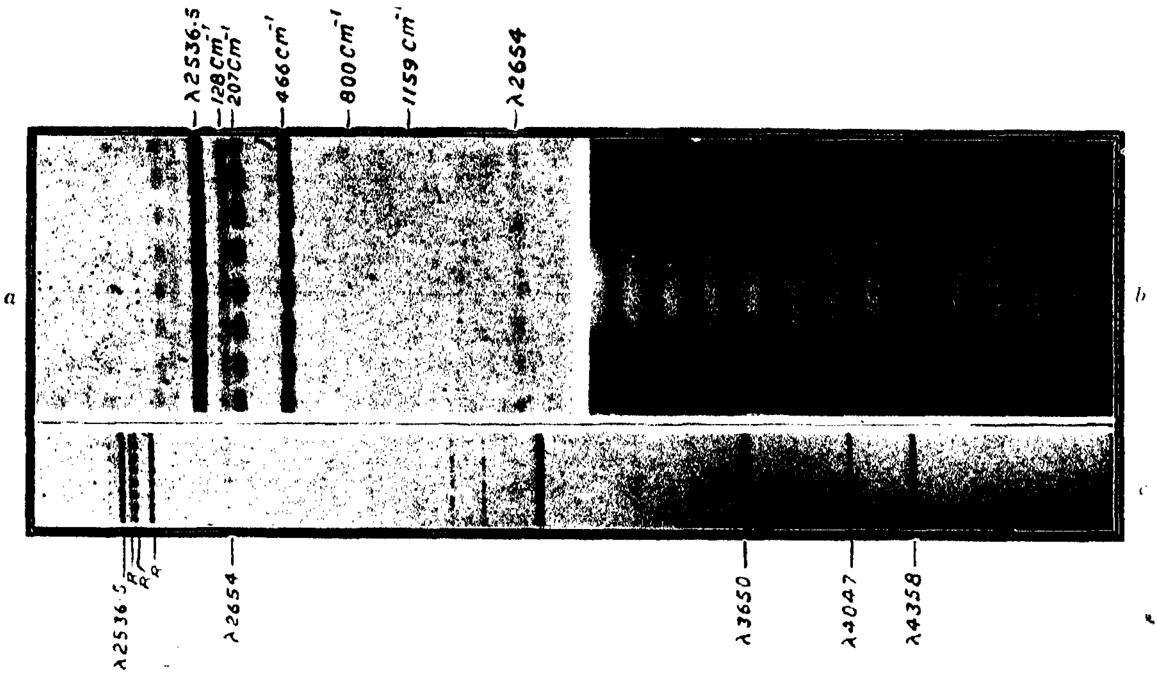

FIG. 1

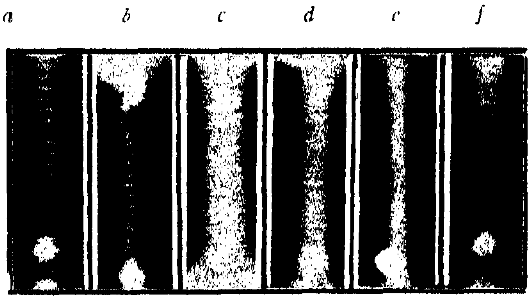

FIG. 2

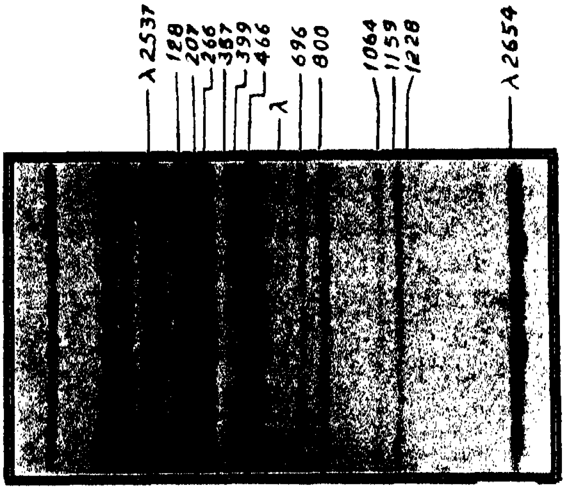

FIG. 3

subgroups are of uniform intensity irrespective of their depolarisation values. This result, which is in complete conformity with theory, verifies for the first time the selection rules for polarised light travelling along the optic axis of quartz—the optical activity itself, usually a disturbing factor, being made use of for the purpose. That the band widths of the Raman lines and that of the exciting line are identical is interesting. The variation in band width of some intense mercury lines, recorded due to inclusions present in the crystal used, shows clearly the rapid increase in the rotatory power of quartz in the ultraviolet.

The obliteration of the banding when the incident light travels at small angles to the optic axis of a clear and transparent sphere of quartz is recorded and a theoretical explanation is given.

Note added in Proof.—Since sending the paper for publication, the author has obtained an intense spectrogram of the scattering in quartz, giving an exposure of the order of 7 days and using a slit width of 0·08 mm. An enlargement of the same is reproduced in Fig. 3, Plate VII. It shows clearly all the principal Raman lines of quartz except 1082 cm.$^{-1}$ line. Of these, three lines (207, 357 and 460 cm.$^{-1}$) belonging to Class A exhibit the banding, while the rest—128, 266, 399, 696, 800, 1063, 1159 and 1228 cm.$^{-1}$ lines—are of uniform intensity. The 266 cm.$^{-1}$ line appears to have a trace of banding, but it is due only to the halation produced by the bands of the intense adjacent 207 cm.$^{-1}$ line. The 1082 cm.$^{-1}$ Raman line, coming under the symmetric Class A, has zero intensity for the particular direction of excitation used in the present investigation (Saxena, 1940) and hence, is not recorded.

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DESCRIPTION OF PLATE

FIG. 1 *b*.	Scattering of a clear sphere of quartz traversed by plane-polarised λ 2537 along optic axis.
FIG. 1 *c*.	Spectrum of scattering of quartz traversed by plane polarised light along the optic axis.
FIG. 1 *a*.	Enlargement of Fig. 1 *c* showing the portion between λ 2537 and λ 2654.
FIG. 2 *a*.	Same as 1 *b*.
FIG. 2 *b*.	Incident light inclined at 4° to the optic axis.
„ 2 *c,d,e*	Incident light inclined at 8° to the optic axis for three different angles of convergence of the beam.
FIG. 2 *f*.	Incident light inclined at 10° to optic axis. Fairly wide beam.
FIG. 3.	Same as Fig. 1 *a*. Intense picture.

THE α–β TRANSFORMATION IN QUARTZ

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IT is well known that quartz undergoes a sudden polymorphic transition at 575° C. from the lower or α- to the high or β-modification, when many of its physical properties undergo a remarkable reversible change. Jay (1933), for example, has shown that the coefficient of thermal expansion as measured both perpendicular and parallel to the optic axis increases anomalously above 200° C. and becomes infinite at about 575° C. The piezo-electric activity of the crystal also falls rapidly as the critical temperature is approached and disappears altogether at the transition point (Pitt and McKinely, 1936). A rapid decrease has also been reported in the measured Young's modulus of the crystal at and preceding 575° C. (Perrier and Mandrot, 1923). The most important change accompanying the transformation is perhaps the increase in symmetry of the crystal, for while α-quartz is trigonal, β-quartz has been shown to possess hexagonal symmetry. This increased symmetry should manifest itself in the Raman spectrum of β-quartz by causing notable variations, especially the disappearance of some of the lines from the spectrum of α-quartz. It is therefore of great interest to investigate the Raman spectrum of quartz just below and above the α-β transition temperature, as it would throw some light on the nature of the transformation.

Although many investigations have been made by various authors on the Raman spectrum of quartz and its variations with temperature (for a review, see Narayanaswamy, 1947) the spectrum of β-quartz has not been obtained so far. This is mainly due to the well-known behaviour of quartz on heating to about 575° C. when the crystal breaks up invariably into fragments in spite of the usual experimental precautions. Nedungadi (1940) was able to record the spectra at temperatures up to 510° C. above which he found that the crystal fell to pieces. The same difficulty was also experienced by the present author in the course of earlier studies (Narayanaswamy, 1947). The difficulties have been overcome now by the use of thin plates as suggested by Sir C. V. Raman to whom the author's thanks are due, and the Raman spectrum of quartz at temperatures above 575° C. has been successfully photographed and the results are given in this paper. The breaking was evidently due to the use of thick specimens in earlier investigations,

2. EXPERIMENTAL DETAILS

Using a thin crystal plate about 1 cm. × 1 cm. × 2 mm. and increasing the temperature gradually, it was found that the transition temperature could be safely exceeded without damage to the crystal. The specimen was mounted inside a specially designed heater which was cylindrical in shape. To ensure uniform heating, the heating coil was wound both at the top and bottom portions of the hollow cylinder leaving a gap in the middle. In this gap, two holes were made to serve as windows for illumination and observation. The temperature of the heater was measured by means of a nichrome-constantan thermocouple in conjunction with a calibrated millivoltmeter. The heating current was drawn directly from the mains through a series of resistances.

The intense λ 2537 resonance radiation of the mercury arc was used for exciting the spectra, employing the Hilger E3 medium quartz spectrograph. Since the crystal used was necessarily thin, exposures of the order of 10–12 hours were found to be necessary to obtain reasonably intense spectrograms with a slit width of 0·04 mm.

3. RESULTS

In continuation of the previous work by the author on quartz, the Raman spectrum was photographed at 470° C. and 550° C. below the transi-

TABLE I. *Variations in frequency shift and width of the Raman lines in quartz at different temperatures*

α-quartz						β-quartz	
27° C. room temperature		470° C.		550° C.		660° C.	
Position cm.$^{-1}$	Width cm.$^{-1}$	Position cm.$^{-1}$	Width cm.$^{-1}$	Position cm.$^{-1}$	Width cm.$^{-1}$	Position cm.$^{-1}$	Width cm.$^{-1}$
128	8·5	106	30	101	36	97	37
207	18·0	170	~ 75	120–200		..	
265	3·5	253	9	251	14	250	15
357	3·0	351	12	350	14	..	
395	3·5	396	17	398	18	395	17
403	3·5						
466	12·0	456	37	454	45	452·5	50
695	6·0	686	12	686	14	~ 686	14
795	4·0	796	19	794	22	792	20
805	4·0						
1064	5·0	1074	12	1072	14	~ 1060	
1083	5·0						
1160		1155	14	1154	19	~ 1154	20
1228	5·0	1224	14	1223		..	

tion point, and at 660° C. above it. Typical spectrograms taken at these temperatures are reproduced on Fig. 1 in plate along with the spectrum of quartz at room temperature. The microphotometer records of the spectra at room temperature, 550° C. and 660° C. are shown in Fig. 2. The measured frequency shifts are put down in Table I.

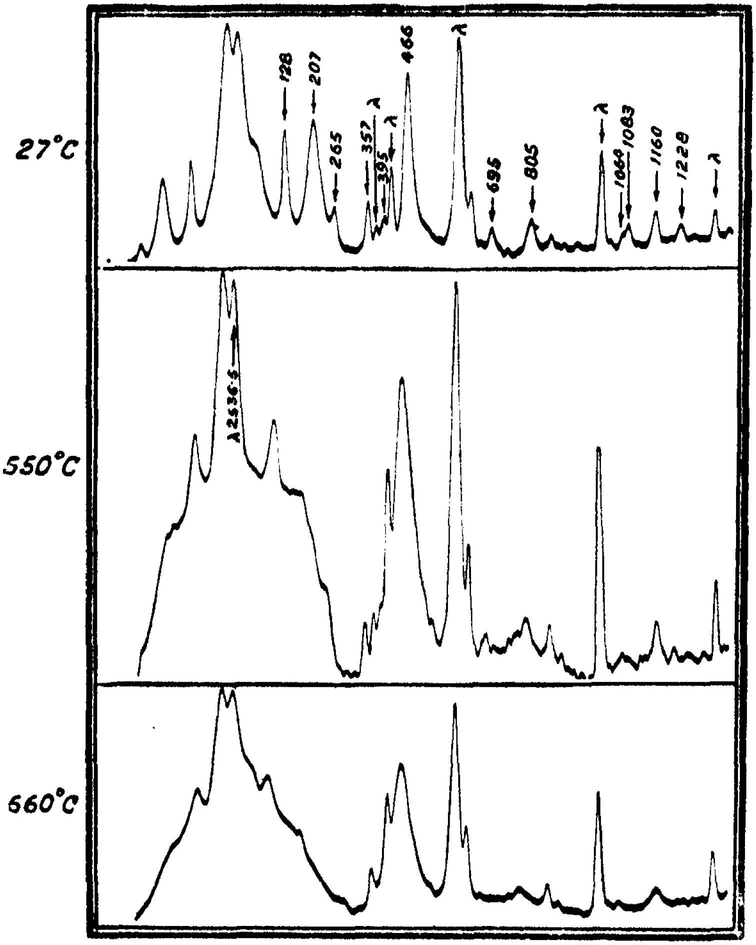

Fig. 2. α—β Transformation in quartz. Microphotometer records of the Raman spectrum of quartz at various temperatures.

The most important feature noticed in the Raman spectrum above the transition temperature is the decrease in the number of frequency shifts. There are no lines corresponding to 207, 357 and 1228 cm.$^{-1}$, although they are present just below that temperature. According to Saxena's (1940) analysis, α-quartz has four frequencies coming under the symmetric class and 8 under the degenerate class. He had identified the lines 207, 357, 466 and 1083 cm.$^{-1}$ under the symmetric class. Two of these oscillations, *viz.*, 207 and 357 cm.$^{-1}$ are definitely absent in the spectrum of β-quartz. Regarding the 1083 cm.$^{-1}$ line it is difficult to say whether it has disappeared or merged with the 1063 cm.$^{-1}$ line, but it is very likely it has also faded out. The anomalous behaviour of the 207 cm.$^{-1}$ line which broadens out enormously with rising temperature, drew the attention of Raman and Nedungadi (1940) who suggested that this has a special importance in the α-β transformation in quartz. The disappearance of the line above the transition temperature fully supports their suggestion.

Seven out of the eight lines coming under the degenerate class are also present in the Raman spectrum of β-quartz. Because of the extreme feebleness of the eighth line, *viz.*, 1228 cm.$^{-1}$, it is most probable that it has failed to appear within the exposures given.

Upto 550° C., a progressive shift in the position and broadening of the lines, though to different extents, is observed. At 660° C., after the transition, even though all the lines are extremely broad and shifted in position, the variation is not of the same order as it should have been if there was no structural change. This is clearly shown in Figs. 3, 4 and 5 where the temperature dependence of the frequency shift and width of the 128, 466 and 1160 cm.$^{-1}$ lines in the range 200–700° C. are graphically represented. The vertical dotted line shows the λ or transition temperature of 575° C. The curve in thick line represents the variation with temperature up to 550° C.

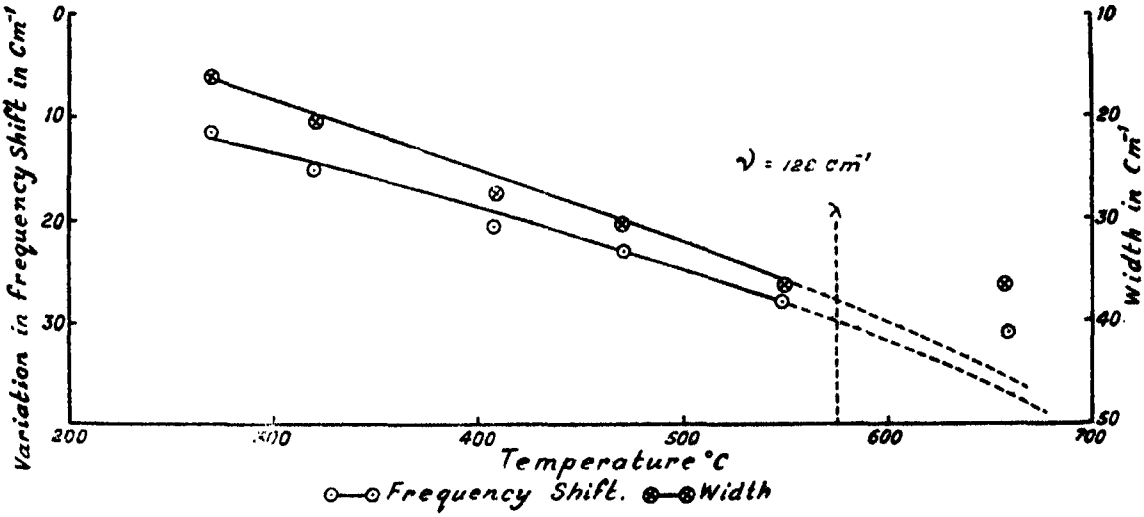

FIG. 3. Temperature dependence of the 128 line.

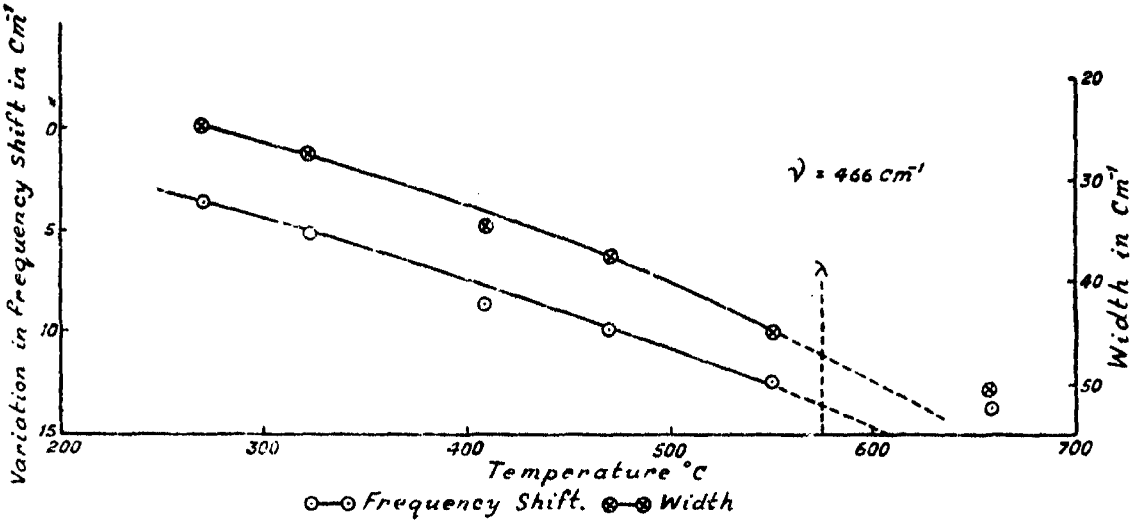

Fig. 4. Temperature dependence of the 466 line.

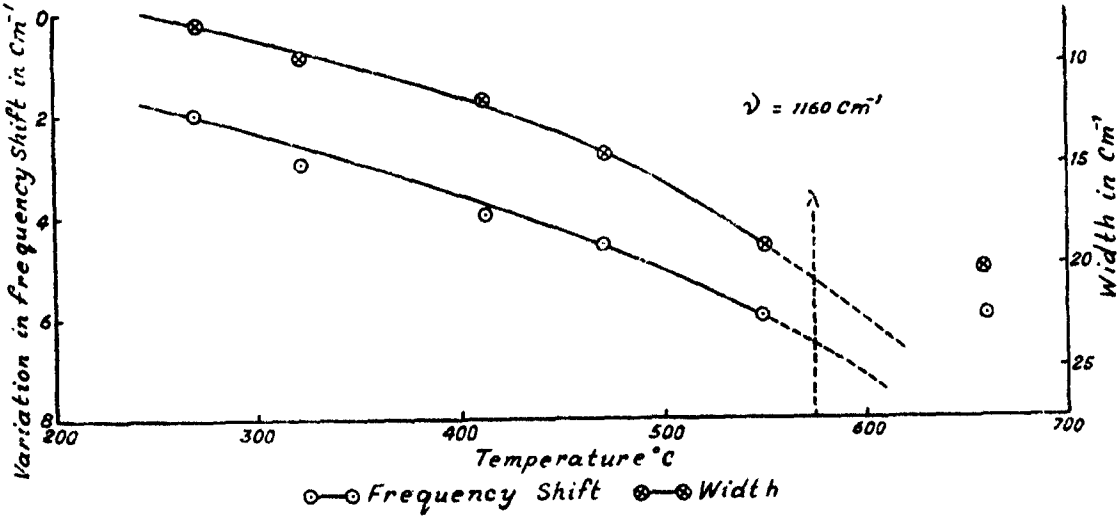

Fig. 5. Temperature dependence of the 1160 line.

The dotted extrapolation shows the variation to be expected beyond that temperature if there was no change in crystal structure. The points outside the curves on the right represent the actually observed variations at 660° C. after the transition.

In conclusion, the author wishes to express his heartfelt thanks to Prof. R. S. Krishnan for his keen interest and guidance in the course of this investigation.

SUMMARY

With the λ 2536·5 resonance radiation of the mercury arc as exciter, the Raman spectrum of β-quartz has been recorded for the first time. Due to the increased symmetry, the spectrum of β-quartz exhibits fewer Raman lines than α-quartz. The variations in frequency shift and width of the Raman lines after the α-β transition point are also found to differ markedly from the corresponding changes observed below the critical temperature.

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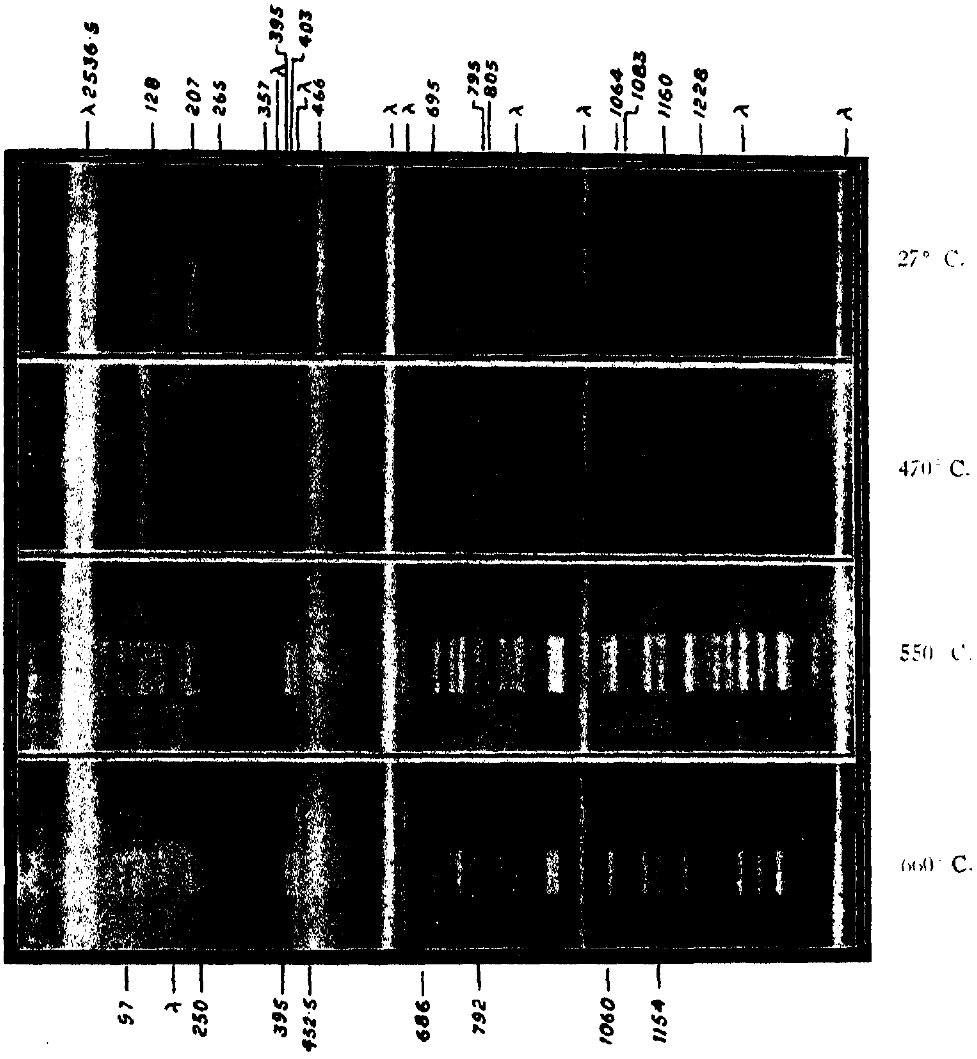

Fig. 1. α-β transformation in quartz. Raman spectrum at different temperatures

A NEW METHOD OF CALCULATING THE PIEZO-ELECTRIC CONSTANTS OF α-QUARTZ*

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Abstract.—A method of calculating the piezo-electric constants of α-quartz is described which consists in determining the electric moment developed by changes of bond-lengths and bond-angles on strain. Considering three atoms P, Q, R, of which P and R are silicon atoms and Q an oxygen atom or *vice-versa*, the electric moment developed on strain may be resolved into moments in the plane PQR and moments perpendicular to this plane. Resolving these moments along the axes of the crystal and summing up for all the forty-two planes in the unit cell, we get the piezo-electric equations and constants of the crystal. The electric moment in the plane is equivalent to the moment produced by the change of bond-length along the direction of the bonds before strain, while for the moment normal to the plane we take the average value, *i.e.*, half the value of the moment normal to the plane when the displacements of the atoms are wholly normal to the plane. The method gives good agreement with the observed values.

INTRODUCTION

THE two piezo-electric constants of α-quartz may be calculated on Born's theory (1924). But the results obtained only give the right order of magnitude. In this paper a new method has been developed for calculating the piezo-electric constants of α-quartz which directly takes into account the structure of the crystal as revealed by X-rays and also enables us to obtain from the crystal structure the two equations which connect the electric moment developed on strain with the components of the strain. These equations are:—

$$\begin{aligned} p_x &= \epsilon_{11}(u_{xx} - u_{yy}) + \epsilon_{41} u_{yz} \\ p_y &= - \epsilon_{41} u_{xz} - \epsilon_{11} u_{xy} \\ p_z &= 0 \end{aligned} \tag{1·1}$$

where p_x, p_y, p_z are the components of the electric moment developed on strain, u_{xx}, u_{xy}, etc., the components of strain and ϵ_{11}, ϵ_{41} the piezo-electric coefficients.

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* A report of this work has appeared in *Nature*, 1948, **161**, 203.

As quartz is a crystal with covalent bindings, the calculations have been made on the supposition that the electric moment developed on strain by a change of length of Si-O bond is $ke\Delta r$ and that produced by a change of angle between two Si-O bonds is $ker\Delta\phi$, where Δr and $\Delta\phi$ represent the change of bond-length and bond-angle on strain and ke represents the charge on an atom where 'k' is a constant whose value is in the neighbourhood of unity. We have first found the moments in the plane of the Si-O bonds and perpendicular to these planes and then resolved them along the axes of the crystal. By summing up for all such planes in the unit cell, we get the piezo-electric coefficients. The above method of approach is more intimately connected with the structure of the crystal. The calculation brings out an interesting result that the changes in bond-length contribute very largely to the longitudinal coefficient ϵ_{11} and nothing to the transverse coefficient ϵ_{41}, which arises entirely from a change of bond angles. The results obtained in this investigation show an agreement with the observed values. Even if we take k as 1, the discrepancy is small, the calculated values for $k = 1$ being $\epsilon_{11} = 6 \cdot 7 \times 10^4$ and $\epsilon_{41} = 1 \cdot 64 \times 10^4$. The best values of these coefficients according to Cady are $5 \cdot 1 \times 10^4$ (ϵ_{11}) and $1 \cdot 23 \times 10^4$ (ϵ_{41}).

2. THE STRUCTURE OF α-QUARTZ

The structure of quartz was first worked out by Bragg and Gibbs (1925, 1926). Each silicon atom appears surrounded by four oxygen atoms and each oxygen atom has two silicon atoms as neighbours. The projection of silicon and oxygen atoms in the basal plane is as shown in Fig. 1. The unit cell in α-quartz is hexagonal and each cell contains six oxygen and three silicon atoms as each silicon atoms is shared between two cells. Using hexagonal axes, the position of nine atoms in the unit cell for right-handed quartz are given as:—

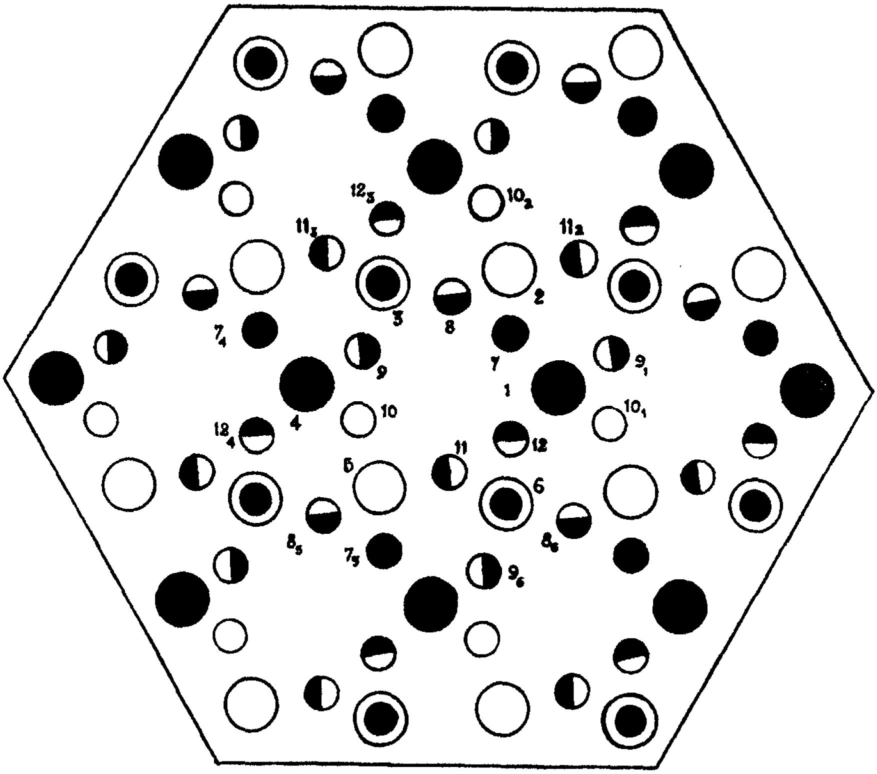
Silicons (in order 1, 3, 5) → $(u, 0, 0)$, $(0, u, \frac{1}{3})$, $(\bar{u}, \bar{u}, \frac{2}{3})$.

Oxygens (in order 7, 8, 9, 10, 11, 12) → $(\bar{x}, y, z)$, $(y, x, z - \frac{2}{3})$, $(\bar{y}, x - y, \frac{1}{3} - z)$, $(\bar{x}, y - x, z - \frac{1}{3})$, $(y - x, \bar{x}, -\frac{1}{3} - z)$, $(x - y, \bar{y}, z)$.

From the X-ray data of Gibb's the author (1944) has calculated

$$u = \cdot 46a,\ x = \cdot 438a,\ y = \cdot 287a,\ z = \cdot 1168c.$$

In Fig. 1 we notice triangular groups of silicon atoms. The triangles are all similar in β-quartz but rotate in opposite senses when the crystal cools to α-quartz. From his X-ray investigations Gibbs found that at room temperature they are rotated by nearly 8° from the positions occupied by them in β-quartz. According to Bragg and Gibbs piezo-electricity arises



● ◉ ○ Si atoms at levels O, $\frac{3c}{9}$, $\frac{6c}{9}$

◓ ◑ ◒ ◐ ○ ● O atoms $\frac{c}{9}$, $\frac{2c}{9}$, $\frac{4c}{9}$, $\frac{5c}{9}$, $\frac{7c}{9}$, $\frac{8c}{9}$

FIG 1

from a distortion of these triangular units on strain. Gibbs obtained a value of the piezo-electric modules δ_{11} by calculating the relative shifts of the centres of gravity of silicon and oxygen units for a pressure of one dyne and multiplying its component parallel to the electric axes by the charge density $4ne$, where n is the number of silicon atoms per c.c. The value of the piezo-electric modulus calculated in this way is 30×10^{-8} which is nearly five times the experimental value. Gibbs has not calculated δ_{41} nor does his method show how the equations (1·1) can be derived from the structure of the crystal. It is to be noted that the piezo-electric moduli δ are related to piezo-electric constants by the relations:—

$$\begin{aligned} \epsilon_{11} &= \delta_{11}(c_{11} - c_{12}) + \delta_{41} c_{14} \\ \epsilon_{41} &= 2\delta_{11} c_{14} + \delta_{41} c_{44}, \end{aligned} \qquad (2\cdot 1)$$

where c_{11}, c_{12}, etc., are the elastic constants.

3. CALCULATION OF THE VARIATION OF BOND LENGTHS AND BOND ANGLES ON STRAIN

Let us now consider the elastic deformation of the crystal. If x, y, z be the rectangular coordinates of a point before it is deformed and $x + u$, $y + v$, $z + w$ after it is deformed, we have (see Love)

$$\begin{aligned} u &= x u_{xx} + (\tfrac{1}{2}u_{xy} - \omega_z)\, y + (\tfrac{1}{2}u_{xz} + \omega_y)\, z \\ v &= (\tfrac{1}{2}u_{xy} + \omega_z)\, x + u_{yy}\cdot y + (\tfrac{1}{2}u_{yz} - \omega_x)\, z \\ w &= (\tfrac{1}{2}u_{xz} - \omega_y)\, x + (\tfrac{1}{2}u_{yz} + \omega_x)\, y + u_{zz}\cdot z \end{aligned} \qquad (3\cdot 1)$$

where u_{xy}, u_{yy}, etc., are strain components and ω_x, ω_y, ω_z are the rotations about the axes. If however there are two points 'P' and 'Q', having coordinates x_1, y_1, z_1 and x_2, y_2, z_2 before strain which change to $x_1 + u_1$, $y_1 + v_1$, $z_1 + w_1$ and $x_2 + u_2$, $y_2 + v_2$, $z_2 + w_2$ after strain, the change in the length of the line PQ after strain is given by:—

$$r\,(l^2 u_{xx}^2 + m^2 u_{yy}^2 + n^2 u_{zz}^2 + lm\, u_{xy} + mn\, u_{yz} + ln\, u_{xz}) \qquad (3\cdot 2)$$

where l, m, n are the direction cosines of a line before strain. Thus we notice that although the direction cosines of a line after strain contain the unknown coefficients ω_x, ω_y, ω_z, the extension of the line after strain is independent of them and is entirely determined by the strain coefficients.

Similarly if P, Q, R be the three points before strain which change to P_1, Q_1, R_1 after strain, the change $\Delta\alpha$ of the angle PQR is also independent of the rotation coefficients ω_x, ω_y, ω_z. For if PQ $= r_1$, QR $= r_2$, PR $= r_3$ and $\angle$PQR $= \alpha$ we have

$$r_3^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\alpha$$

and by differentiating this we obtain

$$r_3\Delta r_3 = r_1\Delta r_1 + r_2\Delta r_2 - (r_1\Delta r_2 + r_2\Delta r_1)\cos\alpha + r_1 r_2 \sin\alpha\cdot\Delta\alpha \quad (3\cdot 3)$$

Since Δr_1, Δr_2, Δr_3 are independent of ω_x, ω_y, ω_z; $\Delta\alpha$ is also independent of them. It is therefore apparent that in a more general elastic deformation the change in the length of a line and change in the angle between two lines can be completely determined without knowing the rotation components ω_x, ω_y, ω_z; but the same is not true for the direction cosines of a given line.

4. CALCULATION OF THE PIEZO-ELECTRIC MOMENT IN THE PLANE OF BONDS AND PERPENDICULAR TO THIS PLANE

In any elastic deformation the displacement of positive and negative charges produces a static electric moment. As quartz is a crystal with covalent bonds, we need consider only close neighbours, *i.e.*, only those silicon and oxygen atoms which are in close neighbourhood and are bonded to each other may be expected to contribute effectively to the electric moment.

A change of the length Δr in the direction of the bond would produce a moment $ke\Delta r$ in that direction where ke is the sharing of charge represented by the bond. In each unit cell there are just twelve positive and twelve negative charges and also twelve Si-O bonds. Therefore if all the bonds were equivalent, each bond will have the same value of k and if the crystal be ionic k will be unity. But since the crystal belongs to the point group D_3, six Si-O bonds will have one value k_1 and another six will have a different value k_2.

As the direction cosines of a bond after strain are not known, it is not possible to resolve the moments along the axis of the crystal. We therefore consider a plane formed by three atoms P, Q, R of which P and R are silicon atoms and Q an oxygen or *vice-versa* so that PQ and QR represent Si-O bonds. Any displacement of these atoms can be resolved into displacement in the plane PQR and displacement perpendicular to the plane. An electric moment will therefore be produced by the displacements in the plane PQR and by those perpendicular to the plane; the total moment being a vector sum of these two moments. These moments can be resolved along the axes of the crystal.

The moments in the plane are due to extensions and contractions along the directions of the bonds before strain. This may be proved easily. The result of the strain is to alter the lengths PQ and QR and the bond angle PQR. If $e\Delta r_1$ and $e\Delta r_2$ represent the moments along PQ and QR, then the resultant moment is

$$e^2(\Delta r_1^2 + \Delta r_2^2 + 2\Delta r_1 . \Delta r_2 . \cos \alpha),$$

where α is the angle PQR. If α is changed into $\alpha + \Delta\alpha$, then the resultant moment will be $e^2(\Delta r_1^2 + \Delta r_2^2 + 2\Delta r_1 . \Delta r_2 . \cos \alpha - 2 . \Delta r_1 . \Delta r_2 . \sin \alpha . \Delta\alpha)$. Now according to (3·2) both Δr_1 and Δr_2 can be expressed in terms of u_{xx} and u_{yy} which are small quantities of the first order whose squares may be neglected. According to (3.3), $\Delta\alpha$ can be expressed in terms of the strain components u_{xx}, u_{yy}, etc. Therefore the last term in the above expression being a small quantity of the third order can be neglected in comparison to the other terms which are of the second order. Hence the moment in the plane PQR is given by terms $ke\Delta r$ along the direction of the bonds PQ and QR before strain.

The moments perpendicular to the plane of bonds may be found from the changes in the angle PQR. In one extreme case the entire change in the angle PQR will be produced by displacements of atoms normal to the plane PQR, and the change of angle in the plane of the bonds PQR will be zero. In this case the moment normal to the plane will be maximum. In the other extreme case the displacements will be wholly in the plane PQR, the moment normal to the plane being zero. In any particular case, the moment perpendicular to the plane of the bonds will lie between these two values. Since the angle change is small and since in finding out the electric moment of the unit cell, the contributions of a large number of planes have to be considered we may take the average value, *i.e.*, half the value of the maximum moment, as the value of the moment normal to the plane.

The moments perpendicular to the plane may be found in the following manner. Suppose the co-ordinates of the atoms P, Q, R are (x_1, y_1, z_1), (x_2, y_2, z_2), (x_3, y_3, z_3), where $z_1 > z_2 > z_3$ so that with respect to Q as the origin, the co-ordinates of P are $(x_1 - x_2, y_1 - y_2, z_1 - z_2)$ and that of R are $(x_3 - x_2, y_3 - y_2, z_3 - z_2)$. After the strain the co-ordinates of P and R will be as given in (3.1) so that with respect to Q the point P will move above the plane PQR and the point R below the plane. If P and R are silicon atoms and Q an oxygen atom, the motion of P will produce a moment which will be opposed to that of R. Suppose that a change in the angle PQR is produced entirely by the displacements normal to the plane. If PQ = QR, draw a line QN perpendicular to PR (Fig. 2). Before strain, $\angle$NQP $= \angle$NQR,

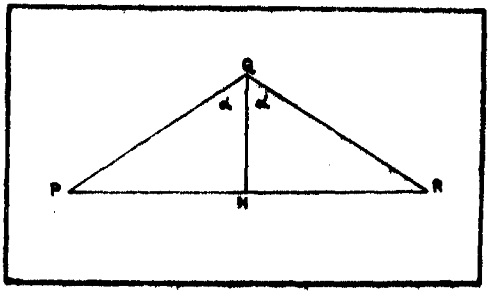


FIG. 2

but after the strain it will not be so. If $\Delta\alpha_1$ be the change in the angle NQP and $\Delta\alpha_2$ in the angle NQR after strain, then $k_1 er \Delta\alpha_1$ will be the moment developed normal to the plane due to the motion of P and $k_2 er\Delta\alpha_2$ due to the motion of Q. The resultant moment is $er(k_1\Delta\alpha_1 - k_2\Delta\alpha_2)$

$$= er\left[\tfrac{1}{2}(k_1 + k_2)(\Delta\alpha_1 - \Delta\alpha_2) + \tfrac{1}{2}(k_1 - k_2)(\Delta\alpha_1 + \Delta\alpha_2)\right] \quad (4.1)$$

Writing $\angle NQP = \angle NQR = \alpha$, $r = PQ = QR$, the changes in PQ and QR as Δr_1 and Δr_2, we have $QN = \nu = r\cos\alpha$.

From triangle NQP, we have $\Delta\nu = \Delta r_1 \cos\alpha - r\sin\alpha\,\Delta\alpha_1$ and from triangle NQR, we have $\Delta\nu = \Delta r_2\cos\alpha - r\sin\alpha\Delta\alpha_2$

$\therefore\ r(\Delta\alpha_1 - \Delta\alpha_2) = (\Delta r_1 - \Delta r_2)\cot\alpha$, which gives $(\Delta\alpha_1 - \Delta\alpha_2)$

If we write $PR = r_3$, and the variation of PR as Δr_3, we get from triangle PQR, $r_3\Delta r_3 = r(\Delta r_1 + \Delta r_2)(1 - \cos 2\alpha) + r^2\sin 2\alpha\cdot(\Delta\alpha_1 + \Delta\alpha_2)$, which gives $(\Delta\alpha_1 + \Delta\alpha_2)$. The average value of the moment normal to the plane will be half of the moment (4.1) which is the moment normal to the plane when the change in the angle PQR is entirely due to the displacements normal to the plane. Its value is therefore

$$\tfrac{1}{2}e\left[\tfrac{1}{2}(k_1+k_2)(\Delta r_1 - \Delta r_2)\cot\alpha + \tfrac{1}{2}(k_1 - k_2)\frac{r_3\Delta r_3 - r(\Delta r_1 + \Delta r_2)(1-\cos 2\alpha)}{r\sin 2\alpha}\right] \quad (4.2)$$

5. ELECTRIC MOMENT OF THE UNIT CELL

As the moments in the planes PQR are along the directions of the bonds PQ and QR and the moments normal to the planes are along the normals, we can resolve the moments along the axes of the crystal. We have now to sum up for all the planes PQR in the unit cell, and divide by the volume of the unit cell to get the electric moment per unit volume. There are six O-Si-O planes at each silicon atom, and there are six silicon atoms in the unit cell. But as each silicon atom is shared between two cells, the contributions of each of the six O-Si-O planes are equally shared between the two cells. In addition the contributions of the six Si-O-Si planes belong entirely to the cell. In summing up for all the planes, the electric moment produced by the displacement of silicon and oxygen atoms is reckoned four times. For example, the displacements of silicon atom (1) and oxygen atom (7) of the unit cell, and consequently the electric moments developed due to their motion, are counted four times if we resolve and sum up the electric moments of the planes (1, 7, 2), (1, 7, 12), and (1, 7, 10_1) and (1, 7, 9_1) which contain the atoms (1) and (7). Hence the moment per unit cell is given by:

$\tfrac{1}{4}$ [$\tfrac{1}{2}$ (moment due to 36 $^{\mathrm{O}\diagdown}\mathrm{Si-O}$ planes)+moments due to 6 Si-O-Si planes].

Let us first consider the moments in the plane which are equivalent to the electric moments along the directions of the Si-O bonds. In the six O-Si-O planes at each silicon atom, there are only four Si-O bonds each of which is reckoned three times in summing up for the six planes. Thus as there are six silicon atoms in the unit cell, we have in all 24 Si-O bonds each of which is reckoned three times in summing up. It is immediately seen (Fig. 1) that twelve of these are identical with the other twelve as they are obtained by a mere translation of the atoms parallel to the electric axes. Hence half the moment in the plane due to thirty-six O-Si-O planes is just equivalent to the electric moment along the directions of the twelve Si-O bonds each of which is reckoned three times. Further the electric moment in the plane due to six Si-O-Si planes are equivalent to those along the twelve Si-O bonds. Thus each Si-O bond is reckoned four times. Hence the moments in the planes per unit cell are just equivalent to the moments $ke\Delta r$ along the twelve Si-O bonds, where Δr is the variation of the length of the Si-O bond.

As the silicon atoms (2), (1), (6) with their associated oxygen atoms have been obtained by a mere translation of the silicon atoms (5), (4), (3) with their associated oxygen atoms, half of the moment due to thirty-six planes is equivalent to the moments due to eighteen O-Si-O planes at silicon atoms (6), (1), (2).

We may now resolve the moments along the axes of the crystal. If (l, m, n) be the direction-cosines of the various Si-O bonds and (p, q, r) of the various normals to the O-Si-O and Si-O-Si planes, V the volume of the unit cell, e the electronic charge, we get

$$p_x = \frac{e}{V}\begin{bmatrix}\text{12 Si-O bonds}\\ \Sigma(k\Delta r\cdot l)\end{bmatrix} + \frac{e}{8V}\Bigg[\begin{matrix}\text{18 O-Si-O and 6 Si-O-Si planes}\\ \Sigma\left\{\tfrac{1}{2}(k_1+k_2)(\Delta r_1-\Delta r_2)\cot\alpha\right.\end{matrix}$$
$$\left. + \tfrac{1}{2}(k_1-k_2)\frac{r_3\Delta r_3 - r(\Delta r_1+\Delta r_2)(1-\cos 2a)}{r\sin 2a}\right\}p\Bigg] \quad (5.1)$$

with similar expressions for p_y and p_z.

This equation gives rise to equations of the form (1·1).

The values of Δr's for the various Si-O bonds in the unit cell have been given by the author (1944). Further the bonds $r_{1,7}$, $r_{1,12}$, $r_{3,9}$, $r_{5,10}$, $r_{3,8}$, $r_{5,11}$ contribute a value $k_1e\Delta r$ to the electric moments and $r_{2,7}$, $r_{6,12}$, $r_{2,8}$' $r_{6,11}$, $r_{4,9}$ and $r_{4,10}$ contribute a value $k_2e\Delta r$.

Knowing the direction cosines of the bonds and assuming that the direction of the moment is from silicon to oxygen we get for the first part in parenthesis in the above expression

$$p_x = a\frac{e}{V}(u_{xx}-u_{yy}) \times 10^{-8} = \lambda(u_{xx}-u_{yy})$$
$$p_y = -a\frac{e}{V}u_{xy} \times 10^{-8} = -\lambda\, u_{xy}$$
$$p_z = 0, \qquad (5.2)$$

where $a = \frac{4\cdot56\, k_1 - \cdot62\, k_2}{(1\cdot588)^2}$, $V = 111\cdot2 \times 10^{-24}$ c.c.

$$e = 4\cdot77 \times 10^{-10}\, e.s.u., \quad \lambda = (7\cdot756\, k_1 - 1\cdot054\, k_2) \times 10^4.$$

Thus it is immediately apparent from these calculations that the moments along Si-O bonds give rise to longitudinal coefficients only.

For finding moments perpendicular to the planes of Si-O bonds we need the expressions

$$\tfrac{1}{2}(k_1 + k_2)(\Delta r_1 - \Delta r_2) \cot \alpha \text{ and}$$

$$\frac{k_1 - k_2}{2r \sin 2\alpha} [r_3 \Delta r_3 - r(\Delta r_1 + \Delta r_2)(1 - \cos 2\alpha)].$$

These along with the direction cosines of the normals to the various planes and the direction cosines of Si-O bonds and the variations of bond lengths are given in the appendix. The moments produced by 18 O-Si-O and six Si-O-Si planes fall into five groups. The moments in each group can be combined with others as such or with signs changed . We have seen before that the moments in the plane of the Si-O bonds do not contribute anything to the transverse piezo-electric coefficient. It may therefore be expected that the moments perpendicular to the plane of Si-O bonds will give rise to the transverse coefficient and will not contribute anything or contribute very little to the longitudinal coefficient. Also the value of k_1 should not be very different from k_2 and should be in the neighbourhood of unity. When this is kept in view there is only one way of combining them. (If we put $k_1 = k_2 = 1$ we find that the contribution of moments perpendicular to the plane of Si-O bonds is very small towards the longitudinal coefficient.) We get

$$p_x = [(-\cdot9988\, k_1 + 1\cdot0806\, k_2)(u_{xx} - u_{yy}) + (2\cdot866\, k_1 + \cdot202 k_2)\, u_{yz}] \frac{e}{8V} \times 10^{-8}$$

$$p_y = [-(-\cdot9988 k_1 + 1\cdot0806 k_2)\, u_{xy} - (2\cdot866 k_1 + \cdot202 k_2)\, u_{xz}] \frac{e}{8V} \times 10^{-8}$$

$$p_z = 0, \qquad (5.3)$$

If the moments perpendicular to the plane of Si-O bonds do not contribute to the longitudinal coefficient we must have

$$\cdot9988 k_1 = 1\cdot0806 k_2 \text{ (or } k_1 = 1\cdot082 k_2)$$

and the resolved parts of these moments along the axes become

$$p_x = [(1\cdot537 k_1 + \cdot1083 k_2)\, u_{yz}] \times 10^4$$

$$p_y = [-(1\cdot537 k_1 + \cdot1083 k_2)\, u_{xz}] \times 10^4$$

$$p_z = \quad 0 \qquad (5.4)$$

The total moments along the axes are the sum of the two expressions (5.2) and (5.4).

$$p_x = [(7\cdot 756k_1 - 1\cdot 054k_2)(u_{xx} - u_{yy}) + (1\cdot 537k_1 + \cdot 1083k_2)\, u_{yz}] \times 10^4$$

$$p_y = -(7\cdot 756k_1 - 1\cdot 054k_2)\, u_{xy} - (1\cdot 537k_1 + \cdot 1083k_2)\, u_{xz}] \times 10^4$$

$$p_z = 0, \tag{5.5}$$

$$\therefore \quad \epsilon_{11} = (7\cdot 756k_1 - 1\cdot 054k_2) \times 10^4$$

$$\epsilon_{41} = (1\cdot 537k_1 + \cdot 1083k_2) \times 10^4 \tag{5.6}$$

Using $\epsilon_{11} = 5\cdot 1 \times 10^4$ we get $k_1 = \cdot 695$, $k_2 = \cdot 752$ and so $\epsilon_{41} = 1\cdot 23 \times 10^4$ which is the observed value

If, however, we put $k_1 = k_2 = 1$ we get $\epsilon_{11} = 6\cdot 78 \times 10^4$ and $\epsilon_{41} = 1\cdot 64 \times 10^4$. Even these values are quite close to observed ones

$$\epsilon_{11} = 5\cdot 1 \times 10^4 \text{ and } \epsilon_{41} = 1\cdot 23 \times 10^4.$$

In this way we derive the equations of the type (1.1) from the structure and obtain satisfactory values of the piezo-electric coefficients. The value of k_1 and k_2 which are in the neighbourhood of ·7 show that the bonds are not ionic. This is also otherwise apparent since quartz is a hard crystal, showing high spectroscopic frequencies and the Si-O-Si angle is not 180°. Further it is also apparent from these calculations that the piezo-electric constants ϵ_{11} and ϵ_{41} are the true structure constants and not the modulii δ_{11} and δ_{41} which depend also on the elastic constants as in (2.1).

6. APPENDIX

The variations in length (Δr) of the various Si-O bonds are given by:

$1\cdot 588\ \Delta r_{1,7} = \cdot 6486u_{xx} + 1\cdot 474u_{yy} + \cdot 397u_{zz} - \cdot 9777u_{xy} - \cdot 7647u_{yz} + \cdot 5074u_{xz}$

$1\cdot 588\ \Delta r_{1,12} =$ same as above with signs of u_{xy} and u_{xz} changed.

$1\cdot 588\ \Delta r_{2,7} = \cdot 0155u_{xx} + 1\cdot 141u_{yy} + 1\cdot 364u_{zz} - \cdot 1288u_{xy} - 1\cdot 248u_{yz} + \cdot 1408u_{xz}$

$1\cdot 588\ \Delta r_{6,12} =$ same as above with signs of u_{xy} and u_{xz} changed.

$1\cdot 588\ \Delta r_{2,8} = \cdot 9720u_{xx} + \cdot 1840u_{yy} + 1\cdot 364u_{zz} + \cdot 4239u_{xy} + \cdot 501u_{yz} + 1\cdot 152u_{xz}$

$1\cdot 588\ \Delta r_{6,11} =$ same as above with signs of u_{xy} and u_{xz} changed.

$1\cdot 588\ \Delta r_{4,9} = \cdot 7468u_{xx} + \cdot 4081u_{yy} + 1\cdot 364u_{zz} + \cdot 5521u_{xy} + \cdot 7461u_{yz} + 1\cdot 009u_{xz}$

$1\cdot 588\ \Delta r_{4,10} =$ same as above with signs of u_{xy} and u_{xz} changed.

$1\cdot 588\ \Delta r_{3,9} = \cdot 4209u_{xx} + 1\cdot 703u_{yy} + \cdot 397u_{zz} + \cdot 8465u_{xy} + \cdot 8219u_{yz} + \cdot 4087u_{xz}$

$1\cdot 588\ \Delta r_{5,10} =$ same as above with signs of u_{xy} and u_{xz} changed.

$1\cdot 588\ \Delta r_{3,8} = 2\cdot 115u_{xx} + \cdot 0083u_{yy} + \cdot 397u_{zz} - \cdot 1323u_{xy} - \cdot 0573u_{yz} + \cdot 9160u_{xz}$

$1\cdot 588\ \Delta r_{5,11} =$ same as above with signs of u_{xy} and u_{xz} changed.

These Δr's are in A.U.

The direction cosines of the various Si-O bonds are:

	$r_{3,8}$	$r_{2,7}$	$r_{1,7}$	$r_{1,12}$	$r_{6,12}$	$r_{5,11}$	$r_{5,10}$	$r_{4,10}$	$r_{4,9}$	$r_{3,9}$	$r_{2,8}$	$r_{6,11}$
l ..	− ·9858	·1206	− ·8054	− ·8054	·1206	1·454	− ·6488	·8642	·8642	− ·6488	1·454	− ·9858
m ..	− ·4290	−1·068	1·214	−1·214	1·068	·091	1·305	− ·6389	·6389	−1·305	− ·091	·4290
n ..	−1·168	1·168	− ·630	·630	−1·168	− ·630	·630	−1·168	1·168	− ·630	·630	1·168
	1·588	1·588	1·588	1·588	1·588	1·588	1·588	1·588	1·588	1·588	1·588	1·588

The values of $\Sigma k\ \Delta r.l$, $\Sigma k\ \Delta r.m$, $\Sigma k\ \Delta r.n$ required for the first part in parenthesis in the expression (5.1) can then be evaluated, and are given in expressions (5.2).

The direction cosines (p, q, r) of the normals to the various planes are:

	1, 7, 12	8_6, 6, 9_6	10_2, 2, 11_2	1, 9_1, 10_1	8, 2, 7	11, 6, 12	12, 1, 10_1	9_6, 6, 11	8, 2, 10_2	7, 2, 11_2	7, 1, 9_1	8_6, 6, 12
p ..	0	·8795	·8795	0	−1·748	−1·748	−1·82	1·254	1·254	·5665	−1·82	·5665
q ..	1·015	·5073	− ·5073	2·02	1·01	−1·01	·3963	−1·379	1·379	1·774	− ·3963	−1·774
r ..	1·956	−1·956	1·956	−1·104	1·104	−1·104	−1·564	1·564	−1·564	1·564	1·564	−1·564
	2·203	2·203	2·203	2·301	2·301	2·301	2·431	2·431	2·431	2·431	2·431	2·431

	12, 1, 9_1	7, 1, 10_1	7, 2, 10_2	9_6, 6, 12	8, 2, 11_2	8_6, 6, 11	1, 7, 2	6, 12, 1	2, 8, 3	5, 11, 6	3, 9, 4	4, 10, 5
p ..	−1·82	−1·82	2·197	2·197	− ·3766	− ·3766	− ·7454	− ·7454	− ·3766	− ·3766	1·122	1·122
q ..	1·485	−1·485	·8338	− ·8338	2·319	−2·319	− ·8646	·8646	−1·077	1·077	− ·2133	·2133
r ..	·535	− ·535	·535	− ·535	− ·535	·535	− ·7135	·7135	·7135	− ·7135	− ·7135	·7135
	2·409	2·409	2·409	2·409	2·409	2·409	1·346	1·346	1·346	1·346	1·346	1·346

The values of

$$\frac{k_1+k_2}{2}(\Delta r_1 - \Delta r_2)\cot\alpha \quad \text{and} \quad \frac{k_1-k_2}{2r\sin 2\alpha}\left[r_3\Delta r_3 - r(\Delta r_1+\Delta r_2)(1-\cos 2\alpha)\right]$$

are given below. The values of the moments p_x, p_y, p_z for the various groups of planes using the second part within brackets in the expression (5.1) are also being given. These values refer only to the moments perpendicular to the various planes given above.

Plane	$\frac{1}{2}(k_1+k_2)(\Delta r_1-\Delta r_2)\cot\alpha$	$\frac{k_1-k_2}{2r\sin 2\alpha}[r_3\Delta r_3-r(\Delta r_1+\Delta r_2)(1-\cos 2\alpha)]$
7, 1, 12	$k_1\{-\cdot 7274u_{xy}+\cdot 3779u_{xz}\}$	0
8_6, 6, 9_6	$k_1\{\cdot 6311(u_{xx}-u_{yy})-\cdot 3644u_{xy}$ $-\cdot 3274u_{yz}+\cdot 1889u_{xz}$	0
10_2, 2, 11_2	same as for 8_6, 6, 9_6 with signs of	u_{xy} and u_{xz} changed

$$p_x=[\cdot 5035\,(u_{xx}-u_{yy})-\cdot 2611u_{yz}]\frac{k_1e}{8V}\times 10^{-8}$$

$$p_y=[-\cdot 5035u_{xy}+\cdot 2611u_{xz}]\frac{k_1e}{8V}\times 10^{-8}$$

$$p_z=\qquad 0;\qquad \cot\alpha=\cdot 5913 \tag{I}$$

9_1, 1, 10_1	$k_2[\cdot 4512u_{xy}+\cdot 8247u_{xz}]$	0
8, 2, 7	$k_2[\cdot 3909(u_{xx}-u_{yy})+\cdot 2258u_{xy}$ $+\cdot 7148u_{yz}+\cdot 4132u_{xz}$	0
11, 6, 12	same as for 8, 2, 7 with signs of	u_{xy} and u_{xz} changed

$$p_x=[-\cdot 5941\,(u_{xx}-u_{yy})-1\cdot 085u_{yz}]\frac{k_2e}{8V}\times 10^{-8}$$

$$p_y=[\cdot 5941u_{xy}+1\cdot 085u_{xz}]\frac{k_2e}{8V}\times 10^{-8}$$

$$p_z=\qquad 0;\ \cot\alpha=\cdot 6491 \tag{II}$$

7, 1, 9_1	$\frac{k_1+k_2}{2}[-\cdot 04752u_{xx}+\cdot 5147u_{yy}$ $-\cdot 467u_{zz}-\cdot 7389u_{xy}-\cdot 7298u_{yz}$ $-\cdot 2432u_{xz}$	$\frac{k_1-k_2}{2}[\cdot 6722u_{xx}-\cdot 1328u_{yy}+\cdot 6616u_{zz}$ $-\cdot 2768u_{xy}-\cdot 6598u_{yz}+\cdot 7125u_{xz}]$
12, 1, 10_1	same as for 7, 1, 9_1 with signs of	u_{xy} and u_{xz} changed
8, 2, 10_2	$\frac{k_1+k_2}{2}[-\cdot 2662u_{xx}+\cdot 7336u_{yy}-\cdot 467u_{zz}$ $-\cdot 6134u_{xy}+\cdot 1584u_{yz}-\cdot 7534u_{xz}]$	$\frac{k_1-k_2}{2}[-1\cdot 069u_{xx}+\cdot 4074u_{yy}+\cdot 6616u_{zz}$ $+\cdot 7266u_{xy}+\cdot 9461u_{yz}-\cdot 2147u_{xz}]$
9_6, 6, 11	same as for 8, 2, 10_2 with signs of	u_{xy} and u_{xz} changed
7, 2, 11_2	$\frac{k_1+k_2}{2}[1\cdot 014u_{xx}-\cdot 5478u_{yy}-\cdot 467u_{zz}$ $+\cdot 1261u_{xy}+\cdot 5751u_{yz}-\cdot 5104u_{xz}]$	$\frac{k_1-k_2}{2}[-\cdot 5899u_{xx}-\cdot 0678u_{yy}+\cdot 6616u_{zz}$ $+1\cdot 017u_{xy}-\cdot 2863u_{yz}-\cdot 9264u_{xz}]$
8_6, 6, 12	same as for 7, 2, 11_2 with signs of	u_{xy} and u_{xz} changed

$$p_x=\Big[\Big(\cdot 269\frac{k_1+k_2}{2}-2\cdot 386\frac{k_1-k_2}{2}\Big)(u_{xx}-u_{yy})$$

$$+\Big(1\cdot 523\frac{k_1+k_2}{2}+1\cdot 829\frac{k_1-k_2}{2}\Big)u_{yz}\Big]\frac{e}{8V}\times 10^{-8}$$

$$p_y=\Big[-\Big(\cdot 269\frac{k_1+k_2}{2}-2\cdot 386\frac{k_1-k_2}{2}\Big)u_{xy}$$

$$-\Big((1\cdot 523\frac{k_1+k_2}{2}+1\cdot 829\frac{k_1-k_2}{2}\Big)u_{xz}\Big]\frac{e}{8V}\times 10^{-8}$$

$$p_z=\qquad 0;\ \cot\alpha=\cdot 767 \tag{III}$$

Plane	$\frac{1}{4}(k_1+k_2)(\Delta r_1-\Delta r_2)\cot\alpha$	$\frac{k_1-k_2}{2r\sin 2\alpha}\,[r_3\Delta r_3-r(\Delta r_1+\Delta r_2)(1-\cos 2\alpha)$
12, 1, 9	$\frac{k_1+k_2}{2}\,[-\cdot 0458u_{xx}+\cdot 4972u_{yy}-\cdot 451u_{zz}$ $+\cdot 1986u_{xy}-\cdot 7049u_{yz}-\cdot 7071u_{zx}]$	$\frac{k_1-k_2}{2}\,[\cdot 6507u_{xx}+\cdot 6631u_{yy}-1\cdot 304u_{zz}$ $+\cdot 7396u_{xy}+\cdot 6725u_{yz}+\cdot 1655u_{zx}]$
$7, 1, 10_1$	same as for $12, 1, 9_1$ with signs of	u_{xy} and u_{zx} changed
$7, 2, 10_2$	$\frac{k_1+k_2}{2}\,[\cdot 1891u_{xx}+\cdot 2621u_{yy}-\cdot 451u_{zz}$ $-\cdot 3347u_{xy}+\cdot 9656u_{yz}-\cdot 2564u_{zx}]$	$\frac{k_1-k_2}{2}\,[\cdot 01934u_{xx}+1\cdot 29u_{yy}-1\cdot 304u_{zz}$ $-\cdot 3737u_{xy}-\cdot 4789u_{yz}-\cdot 4995u_{zx}]$
9_6, 6, 12	same as for $7, 2, 10_2$ with signs of	u_{xy} and u_{zx} changed
$8, 2, 11_2$	$\frac{k_1+k_2}{2}\,[\cdot 5332u_{xx}-\cdot 0827u_{yy}-\cdot 451u_{zz}$ $-\cdot 136u_{xy}-\cdot 2604u_{yz}-\cdot 9647u_{zx}]$	$\frac{k_1-k_2}{2}\,[1\cdot 299u_{xx}+\cdot 0145u_{yy}-1\cdot 304u_{zz}$ $+\cdot 3763u_{xy}-\cdot 1934u_{yz}+\cdot 6637u_{zx}]$
8_6, 6, 11	same as for $8, 2, 11_2$ with signs of	u_{xy} and u_{zx} changed

$$p_x = \left[\left(\cdot 2476\,\frac{k_1+k_2}{2} - 1\cdot 355\,\frac{k_1-k_2}{2}\right)(u_{xx}-u_{yy}) + \left(2\cdot 908\,\frac{k_1+k_2}{2} - 1\cdot 83\,\frac{k_1-k_2}{2}\right)u_{yz}\right]\frac{e}{8V}\times 10^{-8}$$

$$p_y = \left[-\left(\cdot 2476\,\frac{k_1+k_2}{2} - 1\cdot 355\,\frac{k_1-k_2}{2}\right)u_{xy} - \left(2\cdot 908\,\frac{k_1+k_2}{2} - 1\cdot 83\,\frac{k_1-k_2}{2}\right)u_{xz}\right]\frac{e}{8V}\times 10^{-8}$$

$$p_z = 0;\quad \cot\alpha = \cdot 7408 \qquad \text{(IV)}$$

1, 7, 2	$\frac{k_1+k_2}{2}\,[\cdot 1156u_{xx}+\cdot 0608u_{yy}-\cdot 1766u_{zz}$ $-\cdot 155u_{xy}+\cdot 08824u_{yz}+\cdot 06694u_{zx}]$	$\frac{k_1-k_2}{2}\,[-\cdot 4273u_{xx}+\cdot 4559u_{yy}-\cdot 01524u_{zz}$ $-\cdot 08674u_{xy}-\cdot 4501u_{yz}+\cdot 5509u_{zx}]$
1, 12, 6	same as for 1, 7, 2 with signs of	u_{xy} and u_{zx} changed
2, 8, 3	$\frac{k_1+k_2}{2}\,[\cdot 2087u_{xx}-\cdot 03236u_{yy}$ $-\cdot 1766u_{zz}-\cdot 1016u_{xy}-\cdot 102u_{yz}$ $-\cdot 0431u_{zx}]$	$\frac{k_1-k_2}{2}\,[\cdot 3099u_{xx}-\cdot 2825u_{yy}-\cdot 01524u_{zz}$ $+\cdot 3383u_{xy}-\cdot 2693u_{yz}+\cdot 6751u_{zx}]$
5, 11, 6	same as for 2, 8, 3 with signs of	u_{xy} and u_{zx} changed
3, 9, 4	$\frac{k_1+k_2}{2}\,[-\cdot 0595u_{xx}+\cdot 2364u_{yy}-\cdot 1766u_{zz}$ $+\cdot 05375u_{xy}+\cdot 01385u_{yz}-\cdot 1096u_{zx}]$	$\frac{k_1-k_2}{2}\,[\cdot 1606u_{xx}-\cdot 1289u_{yy}-\cdot 01524u_{zz}$ $+\cdot 4279u_{xy}+\cdot 7150u_{yz}+\cdot 1266u_{zx}]$
4, 10, 5	same as for 3, 9, 4 with signs of	u_{xy} and u_{zx} changed

$$p_x = \left[\left(-\cdot 3443\,\frac{k_1+k_2}{2} + \cdot 564\,\frac{k_1-k_2}{2}\right)(u_{xx}-u_{yy}) + \left(-\cdot 0176\,\frac{k_1+k_2}{2} + 1\cdot 84\,\frac{k_1-k_2}{2}\right)u_{yz}\right]\frac{e}{8V}\times 10^{-8}$$

$$p_y = \left[-\left(-\cdot 3443\,\frac{k_1+k_2}{2} + \cdot 564\,\frac{k_1-k_2}{2}\right)u_{xy} - \left(-\cdot 0176\,\frac{k_1+k_2}{2} + 1\cdot 84\,\frac{k_1-k_2}{2}\right)u_{xz}\right]\frac{e}{8V}\times 10^{-8}$$

$$p_z = 0;\quad \cot\alpha = \cdot 29 \qquad \text{(V)}$$

The sum of the moments along the axes due to these five groups is given in the expressions (5.3). These give the moments along the axes due to the moments perpendicular to the plane of Si-O bonds. The sum of the moments as given in expressions (5.2) and (5.3) or (5.4) gives the total moment along the axes and is given in (5.5). The piezo-electric constants calculated from (5.5) according to (1.1) are given in (5.6).

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VARIATION OF THE PIEZO-ELECTRIC CONSTANTS OF α-QUARTZ WITH TEMPERATURE*

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Abstract.—The method of finding the piezo-electric constants with the help of the variations of bond distances and bond angles on strain has been utilised in finding the variations of the piezo-electric constants ϵ_{11} and ϵ_{41} of α-quartz with temperature. It is found that the variations of ϵ_{11} with temperature can be explained on the basis of the change of co-ordinates with temperature. At 558° C. the silicon atoms are found to occupy the same positions as they do in β-quartz. As the transition temperature is reached, the longitudinal coefficient ϵ_{11} drops to zero, while the transverse coefficient ϵ_{41} decreases by only 15%. The piezo-electric constant of β-quartz has been similarly determined and its value comes out to be $1 \cdot 05 \times 10^4$ for a non-ionic crystal ($k = \cdot 724$) and $1 \cdot 45 \times 10^4$ for an ionic crystal ($k = 1$).

1. Introduction

In the previous paper the authors have found the piezo-electric constants of α-quartz by considering the variations of Si-O bond-lengths and of the Si-O-Si and O-Si-O bond angles in a unit cell in an elastic deformation. The same method has been used to find the variations of the piezo-electric constants ϵ_{11} and ϵ_{41} of α-quartz with temperature, and also to find the piezo-electric constant of β-quartz.

2. Experimental Data on the Variation of the Piezo-Electric Constant with Temperature

According to Perrier (1916) the phenomenon was first independent of temperature and decreased sensibly from 200° C. onwards and finally at 579° C. the piezo-electric liberation of charges ceased suddenly. Dawson (1927) states that the piezo-electric effect increases by 20% from room temperature to 60° C. and then decreases slowly till 300° C. and then rapidly reaches low values at about 480° C. But according to Sculwas-Sorokina (1929) Dawson's results are affected by the electrical conductivity of quartz.

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Andreeff and others (1929) using the quartz resonator method found only a small change of about 10% between 0° C. and 500° C. Freederiscksz and Michailov (1932) have also determined the piezo-electric modulus δ_{41} by the same method. Their results are given below.

T° C.→	150	246	300	380	420	470	502	526	540	552	568
$\delta_{11} \times 10^{+8}$→	6·50	6·68	6·50	6·60	6·50	6·25	6·11	4·50	3·97	3·83	3·3
$S_{11} \times 10^{+12}$→	1·291	1·293	1·298	1·302	1·322	1·355	1·395	1·448	1·484	1·54	1·75
$\epsilon_{11} \times 10^{-4}$→	5·035	5·154	5·007	5·070	4·915	4·607	4·380	3·107	2·675	2·487	1·88

The values of $\epsilon_{11} = \frac{\delta_{11}}{S_{11}}$ given by these authors are only approximate values as the piezo-electric modulus δ_{11} is related to the constant ϵ_{11} by the relation

$$\delta_{11} = \epsilon_{11} (S_{11} - S_{12}) + \epsilon_{41} S_{14}$$

so that

$$\epsilon_{11} = \frac{\delta_{11}}{S_{11}} + e_1 \text{ where } e_1 = \epsilon_{11} \frac{S_{12}}{S_{11}} - \epsilon_{41} \frac{S_{14}}{S_{11}}$$

The value of e_1 at room temperature is only 1/25th of the value of ϵ_{11} and at higher temperatures it is not likely to be very different. We have assumed the values of ϵ_{11} given by these authors, plotted them on a smooth curve, and obtained the following values at various temperatures.

T° C.→	18	118	203	280	366	418	494	525	558	567
ϵ_{11} →	5·1	5·1	5·09	5·08	5·05	4·98	4·15	3·37	2·41	$1{\cdot}89 \times 10^4$

Pitt and Mackinley (1936) have not given any values but they find a weak maximum at 200° C.

There is no data for the variation of ϵ_{41} with temperature.

3. CALCULATION OF THE PIEZO-ELECTRIC CONSTANTS AT VARIOUS TEMPERATURES

For the purpose of these calculations, we must know the co-ordinates of the atoms in α-quartz at various temperatures. Using the hexagonal axes, the positions of the nine atoms in the unit cell have already been given in an earlier paper. These are stated in terms of four parameters—u, x, y, z—where the value of u gives the position of the silicon atoms, and the values of x, y, z, those of the oxygen atoms. If we use rectangular co-ordinates x', y', z' (the horizontal electric axis being the x' axis) we get

$$x' = x - \frac{y}{2};\ y' = \frac{\sqrt{3}}{2} y;\ z' = z.$$

If we write $u = \frac{a}{2} - p$, the position of the silicon atoms become determined if we know p. Gibbs assumes that every oxygen atom is equidistant from its silicon neighbours. If Si-O distance be taken as 'd', and if x', y', z' be the co-ordinates of the reference oxygen atom of the unit cell in rectangular co-ordinates, we can find x', y', if z' be known.

$$y' = \frac{1}{\sqrt{3}}\,\frac{1}{\left(\frac{a}{2}+p\right)}\left\{\left(\frac{a}{2}-3p\right)x' + \left(2ap + \frac{c^2}{9} - \frac{2}{3}cz'\right)\right\}$$

$$x' = \frac{1}{(a^2+12p^2)}\Bigg[3\left(\frac{a^2}{4}-p^2\right)\left(\frac{a}{2}+p\right) - \left(\frac{a}{2}-3p\right)\left(2ap+\frac{c^2}{9}-\frac{2}{3}cz'\right)$$

$$-\sqrt{3}\left(\frac{a}{2}+p\right)\times$$

$$\sqrt{(a^2+12p^2)\left\{d^2-\frac{1}{4}\left(\frac{a^2}{4}+\frac{c^2}{9}+3p^2\right)\right\}-\left(\frac{a^2}{4}+\frac{c^2}{9}+3p^2\right)\left(\frac{c}{3}-2z'\right)^2}\,\Bigg]$$

The distance $q = \sqrt{d^2 - \frac{1}{4}\left(\frac{a^2}{4}+\frac{c^2}{9}+3p^2\right)}$ is the distance of the oxygen atom from the middle point of the line joining the silicon atoms. For β-quartz, $p = 0$, $z' = c/6$; and so $x' = \frac{3a}{8} - \frac{\sqrt{3}}{2}\,q$, $y' = \frac{x'}{\sqrt{3}}$.

The above calculation shows that we need five parameters a, c, p, q, z' to determine the co-ordinates of quartz of various temperatures. The values of a and c at various temperatures are known from the work of Jay (1938) while the values of z' were taken from the work of Gibbs (1925), who measured the intensities of reflection of X-rays from various planes in the crystal, particularly from the (111) plane. To explain the rising part of the curve upto 575° C., Gibbs has given another curve indicating the position of the oxygen planes relative to the silicon planes. From this curve the co-ordinates of the various oxygen atoms were determined, but the shape of the curve beyond 525° C. is not definite. We have no data for the variation of p and q with temperature. From the co-ordinates of α- and β-quartz as obtained from Gibbs' data, we find that the Si-O distance in α-quartz is the same as in β-quartz. We therefore assume that it does not vary with temperature and take it as $1{\cdot}5917$ ($d^2 = 2{\cdot}5337$) for the purpose of our calculations. We are now left with only one parameter p and this was determined with reference to the variation of ϵ_{11} with temperature. Using a particular value of p and z' we can calculate x' and y' from the formulæ given before.

The values of ϵ_{41} have been calculated for the room temperature and for 567° C. while ϵ_{11} has been calculated for all the temperatures. The calculations for ϵ_{41} are very long and tedious, and so they have been made for two temperatures only as shown.

T° C.	'a' A.U.	'c' A.U.	'p' A.U.	'x'' A.U.	'y'' A.U.	'z'' A.U.	$\epsilon_{11} \times 10^{-4}$	$\epsilon_{41} \times 10^{-4}$
18	4·9030	5·3930	·1989	1·443	1·214	·634	5·11	1·23
567	4·9685	5·4355	0	1·496	1·012	·730	1·85	1·08

The values of k_1 and k_2 calculated on the basis that the moments perpendicular to the plane of the bonds give no contribution to the longitudinal piezo-electric coefficient ϵ_{11} are $k_1 = \cdot 752$ and $k_2 = \cdot 695$ at 18° C. and $k_1 = \cdot 724$ and $k_2 = \cdot 757$ at 567° C. There is a certain degree of inexactness in these calculations due to the fact that both z' and ϵ_{11} are not correctly known. As is to be expected, we see that both k_1 and k_2 tend to become equal at 567° C. For the intervening temperatures we have calculated ϵ_{11} by assuming a proper value of 'p'. We have assumed $k_1 = \cdot 752$ and $k_2 = \cdot 659$ for all the temperatures. As already explained this is not strictly true for higher temperatures, but the calculations enable us to explain the fact that the progressive diminution of ϵ_{11} with temperature can be explained by a change of co-ordinates with temperature.

T° C.	'a' A.U.	'c' A.U.	'p' A.U.	'x'' A.U.	'y'' A.U.	'z'' A.U.	$\epsilon_{11} \times 10^{-4}$ Cal.	$\epsilon_{11} \times 10^{+1}$ Obs.
18	4·9030	5·3930	·1989	1·4430	1·2140	·6340	5·11	5·10
118	4·9102	5·3982	·2000	1·4540	1·2200	·6365	5·08	5·10
203	4·9172	5·4027	·2100	1·4690	1·2320	·6380	5·04	5·09
280	4·9245	5·4069	·2200	1·4840	1·2460	·6400	4·97	5·08
366	4·9334	5·4129	·2200	1·4990	1·2520	·6415	4·92	5·05
418	4·9396	5·4163	0·230	1·5170	1·2640	·6430	4·82	4·92
494	4·9503	5·4241	·1000	1·5010	1·1630	·6460	4·16	4·15
525	4·9560	5·4276	·0100	1·5150	1·0980	·6500	3·30	3·37
558	4·9642	5·4338	·0000	1·4950	1·0240	·7150	2·34	2·41
567	4·9685	5·4355	·0000	1·4960	1·0120	·7300	1·85	1·88

4. DISCUSSION

Although the co-ordinates given above are only approximately correct, one point which can be definitely stated is that for 558° C. and 567° C. the value of 'p' is zero. This means that at these temperatures the silicon atoms occupy the same positions as they do in β-quartz. It is also clear that there is a general expansion of the lattice upto 400° C. after which the silicon atoms change their positions rather rapidly and occupy the same positions as they do in β-quartz; it is likely that this condition also exists at 525° C. But the oxygens and silicons do not move appreciably along the 'c' axis upto 558° C. After this the oxygens move appreciably, rather rapidly, and further diminution in ϵ_{11} is due to their motion. From the room temperature to 567° C., the total change in the oxygen positions along the 'c' axis does not exceed ·066 A.U. The oxygens lie at $z' = \cdot 73$ at 567° C. while in β-quartz they lie midway between the silicon planes at $z' = c/6 = \cdot 902$ A.U. The change of ·17 A.U. takes place very close to the critical temperature, and some may take place at the critical temperature itself. An absorption of 4 grs.-calories of heat has been observed by Perrier and Wolfers (1920) at the transition temperature.

A study of the Raman spectra of α-quartz by the author (1940) has brought out the interesting fact that the lines which broaden most with temperature are those in which the movements of atoms are confined to the basal plane, while the lines in which the movements are perpendicular to the basal plane remain practically sharp even at higher temperatures. Of those lines which broaden most with temperature, the line 207 shows the phenomena to a remarkable extent, and the vibration is mostly due to the motion of the silicon atoms in the basal plane. These observations are in general agreement with the observations made above about the motions of the silicon and oxygen atoms. It is possible that the large displacements of the silicon atoms in the basal plane with temperature lead to large amplitudes of vibration of these atoms which gives rise to broadening ; while perpendicular to the basal plane the displacements of atoms are not large enough to give rise to any anharmonicity, in the vibrations.

5. CALCULATION OF THE PIEZO-ELECTRIC CONSTANT ϵ_{41} OF β-QUARTZ

The structure of β-quartz has been investigated by Bragg and Gibbs (1925) and Wyckoff (1926). Using the values 'a' = 5·01 A.U. and 'c' = 5·466 (Jay, 1933 and Landolt Tables) and the value of $q = \cdot 35$ A.U. (Bragg and Gibbs, 1925) we get

$$u = \cdot 5\,a,\ x = \cdot 2094\,a,\ y = -\cdot 2101\,a,\ z = c/6$$

which agree with those given in Landolt's tables.

The calculations for β-quartz are shown in the Appendix. The method of procedure is just the same as in α-quartz. Resolving the moments in the direction of the Si-O bonds along the axes, we get

$$\begin{aligned} p_x &= \cdot 897\,(k_1 - k_2)\,(u_{xx} - u_{yy}) \cdot (e/\mathrm{V}) \times 10^{-8} \\ p_y &= -\cdot 897\,(k_1 - k_2)\,(u_{xy}) \cdot (e/\mathrm{V}) \times 10^{-8} \\ p_z &= 0 \end{aligned} \tag{5.1}$$

As the coefficient of u_{yz} is zero, the moments in the plane of the Si-O bonds give no contribution to the transverse coefficient ϵ_{41}.

The moments perpendicular to the plane of the Si-O bonds when resolved along the axes give

$$\begin{aligned} p_x &= [-\cdot 6838\,(k_1-k_2)(u_{xx}-u_{yy})+2\cdot 879\,(k_1+k_2)/2\cdot u_{yz}]\,(e/8\mathrm{V})\times 10^{-8} \\ p_y &= [\quad \cdot 6838\,(k_1-k_2)(u_{xy})-2\cdot 879\,(k_1+k_2)/2\cdot u_{xz}]\,(e/8\mathrm{V})\times 10^{-8} \\ p_z &= \qquad 0 \end{aligned} \tag{5.2}$$

If we assume, as in α-quartz, that the moments perpendicular to the plane of the bonds give no contribution to the longitudinal coefficient ϵ_{11} we must have $k_1 = k_2$. This is also otherwise evident, for β-quartz is a hexagonal crystal so that both x and y axes are axes of two-fold symmetry. All the Si-O bonds must therefore be of the same type, so that $k_1 = k_2$. The above assumption is therefore justified. Since $k_1 = k_2$, we get

$$\epsilon_{11} = 0 \text{ and } \epsilon_{41} = 2\cdot 879\,k_1\cdot(e/8\mathrm{V})\times 10^{-8} \tag{5.3}$$

It has been shown before that in α-quartz, k_1 becomes nearly equal to k_2 near the transition temperature, and in β-quartz it is so. We therefore take $k_1 = \cdot 724$ in β-quartz which is the mean of the values of k_1 and k_2 in α-quartz. Since the volume of the unit-cell in β-quartz is $118\cdot 8\times 10^{-24}$ c.c. we get $\epsilon_{41} = 1\cdot 05\times 10^4$.

If, however, we take $k_1 = k_2 = 1$, we get $\epsilon_{41} = 1\cdot 45\times 10^4$. Therefore, for β-quartz, $\epsilon_{11} = 0$ and $\epsilon_{41} = 1\cdot 05\times 10^4$. Thus in passing from α-quartz to β-quartz, ϵ_{11} drops to zero, while ϵ_{41} diminishes by nearly 15%. Using $c_{44} = 3\cdot 58\times 10^{11}$ (Kammer and Atanasoff, 1942) and $c_{14} = 0$, we get $\delta_{41} = \frac{\epsilon_{41}}{c_{44}} = 2\cdot 93\times 10^{-8}$.

6. APPENDIX

The Δr's for the various Si-O bonds are given by:

$$\begin{aligned} 1\cdot 587\,\Delta r_{1,7} = {} & \cdot 8641\,u_{xx}+\cdot 8275\,u_{yy}+\cdot 83\,u_{zz}-\cdot 8457\,u_{xy} \\ & -\cdot 8287\,u_{yz}+\cdot 8468\,u_{xz} \end{aligned}$$

$1\cdot 587\,\Delta r_{1,12}$ = same as above with signs of u_{xy} and u_{xz} changed.

$$\begin{aligned} 1\cdot 587\,\Delta r_{2,7} = {} & \cdot 1043\,u_{xx}+1\cdot 587\,u_{yy}+\cdot 83\,u_{zz}-\cdot 4068\,u_{xy} \\ & -1\cdot 149\,u_{yz}+\cdot 2942\,u_{xz} \end{aligned}$$

$1\cdot 587\,\Delta r_{6,12}$ = same as above with signs of u_{xy} and u_{xz} changed.

$$\begin{aligned} 1\cdot 587\,\Delta r_{2,8} = {} & 1\cdot 569\,u_{xx}+\cdot 1225\,u_{yy}+\cdot 83\,u_{zz}+\cdot 4384\,u_{xy} \\ & +\cdot 3188\,u_{yz}+1\cdot 141\,u_{xz} \end{aligned}$$

$1\cdot 587\,\Delta r_{6,11}$ = same as above with signs of u_{xy} and u_{xz} changed.

$$1\cdot587\,\Delta r_{3,8} = 1\cdot569\,u_{xx} + \cdot1225\,u_{yy} + \cdot83\,u_{zz} - \cdot4384\,u_{xy} - \cdot3188\,u_{yz} + 1\cdot141\,u_{xz}$$

$1\cdot587\,\Delta r_{6,11}$ = same as above with signs of u_{xy} and u_{xz} changed.

$$1\cdot587\,\Delta r_{3,9} = \cdot1043\,u_{xx} + 1\cdot587\,u_{yy} + \cdot83\,u_{zz} + \cdot4068\,u_{xy} + 1\cdot149\,u_{yz} + \cdot2942\,u_{xz}$$

$1\cdot587\,\Delta r_{5,10}$ = same as above with signs of u_{xy} and u_{xz} changed.

$$1\cdot587\,\Delta r_{4,9} = \cdot8641\,u_{xx} + \cdot8275\,u_{yy} + \cdot83\,u_{zz} + \cdot8457\,u_{xy} + \cdot8287\,u_{yz} + \cdot8468\,u_{xz}$$

$1\cdot587\,\Delta r_{4,10}$ = same as above with signs of u_{xy} and u_{xz} changed.

The direction-cosines of the various Si-O bonds are:

	$r_{1,7}$	$r_{2,7}$	$r_{2,8}$	$r_{3,8}$	$r_{3,9}$	$r_{4,9}$	$r_{4,10}$	$r_{5,10}$	$r_{5,11}$	$r_{6,11}$	$r_{6,12}$	$r_{1,12}$
l ..	$-\cdot9296$	$\cdot3229$	$-1\cdot252$	$+1\cdot252$	$-\cdot3229$	$\cdot9296$	$\cdot9296$	$-\cdot3229$	$+1\cdot252$	$-1\cdot252$	$\cdot3229$	$-\cdot9296$
m ..	$\cdot9097$	$-1\cdot26$	$-\cdot35$	$-\cdot35$	$-1\cdot26$	$\cdot9097$	$-\cdot9097$	$1\cdot26$	$\cdot35$	$\cdot35$	$1\cdot26$	$-\cdot9097$
n ..	$\frac{-\cdot911}{1\cdot587}$	$\frac{\cdot911}{1\cdot587}$	$\frac{-\cdot911}{1\cdot587}$	$\frac{\cdot911}{1\cdot587}$	$\frac{-\cdot911}{1\cdot587}$	$\frac{\cdot911}{1\cdot587}$	$\frac{-\cdot911}{1\cdot587}$	$\frac{\cdot911}{1\cdot587}$	$\frac{-\cdot911}{1\cdot587}$	$\frac{\cdot911}{1\cdot587}$	$\frac{-\cdot911}{1\cdot587}$	$\frac{+\cdot911}{1\cdot587}$

As before we assign to the bonds $r_{1,7}$, $r_{1,12}$, $r_{3,8}$, $r_{3,9}$, $r_{5,10}$, $r_{6,11}$ the value of the charge $k_1\cdot e$ and to the remaining a value $k_2\cdot e$. The moments along the bonds may now be resolved along the axes. The result is given in (5.1).

The direction-cosines of the normals to the various planes formed by the various Si-O bonds are:

	$7, 1, 10_1$	$12, 1, 9_1$	$8, 2, 11_2$	$8_6, 6, 11$	$7, 2, 10_2$	$9_6, 6, 12$	$1, 7, 2$	$6, 12, 1$	$2, 8, 3$	$5, 11, 6$	$3, 9, 4$	$4, 10, 5$
p ..	$-\cdot9097$	$-\cdot9097$	$-\cdot35$	$-\cdot35$	$1\cdot26$	$1\cdot26$	$-\cdot3189$	$-\cdot3189$	$\cdot6380$	$\cdot6380$	$-\cdot3189$	$-\cdot3189$
q ..	$-\cdot9296$	$\cdot9296$	$1\cdot252$	$-1\cdot252$	$\cdot3229$	$-\cdot3229$	$\cdot5527$	$-\cdot5527$	0	0	$-\cdot5527$	$\cdot5527$
r ..	$\frac{0}{1\cdot301}$	$\frac{0}{1\cdot301}$	$\frac{0}{1\cdot301}$	$\frac{0}{1\cdot301}$	$\frac{0}{1\cdot301}$	$\frac{0}{1\cdot301}$	$\frac{\cdot8778}{1\cdot085}$	$\frac{-\cdot8778}{1\cdot085}$	$\frac{-\cdot8778}{1\cdot085}$	$\frac{\cdot8778}{1\cdot085}$	$\frac{\cdot8778}{1\cdot085}$	$\frac{-\cdot8778}{1\cdot085}$
	$1, 7, 12$	$10_2, 2, 11_2$	$9_1, 1, 10_1$	$8_6, 6, 9_6$	$8, 2, 7$	$11, 6, 12$	$7, 1, 9_1$	$12, 1, 10_1$	$8, 2, 10_2$	$9_6, 6, 11$	$7, 2, 11_2$	$8_6, 6, 12$
p ..	0	$\cdot7889$	0	$\cdot7889$	$-\cdot7889$	$-\cdot7889$	$-\cdot9110$	$-\cdot9110$	$\cdot4555$	$\cdot4555$	$\cdot4555$	$\cdot4555$
q ..	$\cdot9110$	$-\cdot4555$	$\cdot9110$	$\cdot4555$	$\cdot4555$	$-\cdot4555$	0	0	$\cdot7889$	$-\cdot7889$	$\cdot7889$	$-\cdot7889$
r ..	$\frac{\cdot9097}{1\cdot287}$	$\frac{\cdot9097}{1\cdot287}$	$\frac{-\cdot9097}{1\cdot287}$	$\frac{-\cdot9097}{1\cdot287}$	$\frac{\cdot9097}{1\cdot287}$	$\frac{-\cdot9097}{1\cdot287}$	$\frac{\cdot9296}{1\cdot301}$	$\frac{-\cdot9296}{1\cdot301}$	$\frac{-\cdot9296}{1\cdot301}$	$\frac{\cdot9296}{1\cdot301}$	$\frac{\cdot9296}{1\cdot301}$	$\frac{-\cdot9296}{1\cdot301}$

The values of $\frac{1}{2}(k_1 + k_2)(\Delta r_1 - \Delta r_2)$ cot a and $\frac{k_1 - k_2}{2r \sin 2a}$ $\{r_3 \Delta r_3 - r(\Delta r_1 + \Delta r_2)(1 - \cos 2a)\}$ as well as of the moments perpendicular to the plane of the bonds resolved along the axes are being given below.

Plane	$\frac{1}{2}(k_1+k_2)(\Delta r_1 - \Delta r_2)\cot a$	$\frac{k_1-k_2}{2r \sin 2a}[r_3\Delta r_3 - r(\Delta \gamma_1 + \Delta r_2)(1-\cos 2a)]$
1, 7, 12	$(k_1)\cdot(-\cdot 7690 u_{xy} + \cdot 7698 u_{xz})$	0
10_2, 2, 11_2	$(k_1)\cdot[\cdot 6658(u_{xx} - u_{yz}) + \cdot 3842 u_{yy} - \cdot 6668 u_{yz} - \cdot 385 u_{xz}]$	0
8_6, 6, 9_6	same as for 8_6, 6, 9_6 with signs of u_{xy}	and u_{xz} changed.

$$p_x = k_1[\cdot 8158(u_{xx} - u_{yy}) - \cdot 8172\, u_{yz}]\cdot e/8\mathrm{V} \times 10^{-8}$$

$$p_y = k_1[-\cdot 8158\, u_{xy} + \cdot 8172\, v_{xz}]\cdot e/8\mathrm{V} \times 10^{-8}$$

$$p_z = \qquad 0;\ \cot a = \cdot 7216 \tag{1}$$

9_1, 1. 10_1	$= k_2(\cdot 7690 u_{xy} + \cdot 7698 u_{xz})$	0
8, 2, 7 =	$k_2[\cdot 6658(u_{xx} - u_{yy}) + \cdot 3842 u_{xy} + \cdot 6668 u_{yz} + \cdot 385 u_{xz}$	0
11, 6, 12	same as for 8, 2, 7 with signs of	u_{xy} and u_{xz} changed.

$$p_x = k_2[-\cdot 8158(u_{xx} - u_{yy}) - \cdot 8172\, v_{yz}]\cdot e/8\mathrm{V} \times 10^{-8}$$

$$p_y = k_2[\cdot 8158\, u_{xy} + \cdot 8172\, u_{xz}]\cdot e/8\mathrm{V} \times 10^{-8}$$

$$p_z = \qquad 0;\ \cot a = \cdot 7216 \tag{2}$$

7, 1, 9_1	$\frac{k_1+k_2}{2}[-\cdot 7446 u_{xy} - \cdot 7295 u_{yz}]$	$\frac{k_1-k_2}{2}[\cdot 76 u_{xx} - 1\cdot 492 u_{yy} + \cdot 731 u_{zz} + \cdot 7452 u_{xz}]$
12, 1, 10_1	same as for 7, 1, 9_1 with signs of	u_{xy} and u_{xz} changed
8, 2 10_2	$\frac{k_1+k_2}{2}[-\cdot 6445(u_{xx} - u_{yy}) - \cdot 372 u_{xy} + \cdot 365 u_{yz} - \cdot 6316 u_{xz}]$	$\frac{k_1-k_2}{2}[-\cdot 9291 u_{xx} + \cdot 197 u_{yy} + \cdot 731 u_{zz} + \cdot 9755 u_{xy} + \cdot 646 u_{yz} + \cdot 3725 u_{xz}]$
9_6, 6, 11	same as for 8, 2, 10_2 with signs of	u_{xy} and u_{xz} changed
7, 2, 11_2	$\frac{k_1+k_2}{2}[\cdot 6445(u_{xx} - u_{yy}) + \cdot 372 u_{xy} + \cdot 365 u_{yz} - \cdot 6316 u_{xz}]$	$\frac{k_1-k_2}{2}[-\cdot 9291 u_{xx} + \cdot 197 u_{yy} + \cdot 731 u_{zz} + \cdot 9755 u_{xy} - \cdot 646 u_{yz} - \cdot 3725 u_{xz}]$
8_6, 6, 12	same as for 7, 2, 11_2 with signs of	u_{xy} and u_{xz} changed

$$p_x = \left[-2\cdot 364\,\frac{k_1 - k_2}{2}(u_{xx} - u_{yy}) + 1\cdot 531\,\frac{k_1 + k_2}{2}\,u_{yz}\right]\frac{e}{8\mathrm{V}} \times 10^{-8}$$

$$p_y = \left[2\cdot 364\,\frac{k_1 - k_2}{2}\,u_{xy} - 1\cdot 531\,\frac{k_1 + k_2}{2}\,u_{xz}\right]\frac{e}{8\mathrm{V}} \times 10^{-8}$$

$$p_z = \qquad 0;\ \cot a = \cdot 6987 \tag{3}$$

Plane	$\frac{1}{2}(k_1+k_2)(\Delta r_1-\Delta r_2)\cot\alpha$	$\frac{k-k_2}{2r\sin 2\alpha}[r_3\Delta r_3-r(\Delta r_1+\Delta y_2)(1-\cos 2\alpha)]$
7, 1, 10_1	$\frac{k_1+k_2}{2}[-\cdot 7310u_{yz}+\cdot 7469u_{zx}]$	$\frac{k_1-k_2}{2}[\cdot 763u_{xx}+\cdot 73u_{yy}-1\cdot 493u_{zz}-\cdot 746u_{xy}]$
12, 1, 9_1	same as for 7, 1, 10_1 with signs of	u_{xy} and u_{xz} changed
8, 2, 11_2	$\frac{k_1+k_2}{2}[-\cdot 2812u_{yz}-1\cdot 007u_{zx}]$	$\frac{k_1-k_2}{2}[1\cdot 385u_{xx}+\cdot 1082u_{yy}-1\cdot 493u_{zz}+\cdot 3871u_{xy}]$
8_6, 6, 11	same as for 8, 2, 11_2 with signs of	u_{xy} and u_{xz} chauged
7, 2, 11_2	$\frac{k_1+k_2}{2}[1\cdot 013u_{yz}-\cdot 2595u_{zx}]$	$\frac{k_1-k_2}{2}[\cdot 092u_{xx}+1\cdot 399u_{yy}-1\cdot 493u_{zz}-\cdot 3591u_{xy}]$
9_6, 6, 12	same as for 7, 2, 11_2 with signs of	u_{xy} and u_{xz} changed

$$p_x = \left[-1\cdot 632\,\frac{k_1-k_2}{2}(u_{xx}-u_{yy})+3\cdot 135\,\frac{k_1+k_2}{2}u_{yz}\right]\frac{e}{8V}\times 10^{-8}$$

$$p_y = \left[1\cdot 632\,\frac{k_1-k_2}{2}u_{xy}-3\cdot 135\,\frac{k_1+k_2}{2}u_{xz}\right]\frac{e}{8V}\times 10^{-8}$$

$$p_z = 0;\quad \cot\alpha = \cdot 7002 \tag{4}$$

1, 7, 2	$\frac{k_1+k_2}{2}[\cdot 1033(u_{xx}-u_{yy})-\cdot 05969u_{xy}+\cdot 04341u_{yz}+\cdot 07515u_{zx}$	$\frac{k_1-k_2}{2}[-\cdot 405u_{xx}+\cdot 161u_{yy}+\cdot 236u_{zz}-\cdot 489u_{xy}-\cdot 278u_{yz}+\cdot 160u_{xz}]$
6, 12, 1	same as for 1, 7, 2 with signs of	u_{xy} and u_{xz} changed
2, 8, 3	$\frac{k_1+k_2}{2}[-\cdot 1192u_{xy}-\cdot 08672u_{yz}]$	$\frac{k_1-k_2}{2}[\cdot 444u_{xx}-\cdot 6857u_{yy}+\cdot 236u_{zz}+\cdot 324u_{zx}]$
5, 11, 6	same as for 2, 8, 3 with signs of	u_{xy} and u_{xz} changed
3, 9, 4	$\frac{k_1+k_2}{2}[-\cdot 1033(u_{xx}-u_{yy})-\cdot 05969u_{xy}+\cdot 04341u_{yz}-\cdot 07515u_{zx}]$	$\frac{k_1-k_2}{2}[-\cdot 405u_{xx}+\cdot 161u_{yy}+\cdot 236u_{zz}+\cdot 489u_{xy}+\cdot 278u_{yz}+\cdot 160u_{zx}]$
4, 10, 5	same as for 3, 9, 4 with signs of	u_{xy} and u_{xz} changed

$$p_x = \left[\cdot 9970\,\frac{k_1-k_2}{2}(u_{xx}-u_{yy})-\cdot 153\,\frac{k_1+k_2}{2}u_{yz}\right]\frac{e}{8V}\times 10^{-8}$$

$$p_y = \left[-\cdot 9970\,\frac{k_1-k_2}{2}u_{xy}+\cdot 153\,\frac{k_1+k_2}{2}u_{xz}\right]\frac{e}{8V}\times 10^{-8}$$

$$p_z = 0;\quad \cot\alpha = \cdot 2159 \tag{5}$$

The sum of the moments (1), (2), (3), (4), (5) is given in (5.2) and the piezo-electric constants are calculated in (5.3).

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THE THERMO-OPTIC BEHAVIOUR OF MICA

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1. Introduction

The micas are biaxial crystals of the monoclinic system, and as is well known, they exhibit a perfect cleavage parallel to the (001) plane. It is easy to obtain cleavage laminæ a few hundredths of a millimetre thick. Such laminæ yield striking interference phenomena which have been noticed and discussed by Lord Rayleigh (1906), Chinmayanandam (1914) and Tolansky (1946). These phenomena can be utilised to give a wealth of information regarding the birefringence of the crystal, the topographical details of its cleavage faces and even the lattice spacing perpendicular to the cleavage plane. In the present investigation, the author has employed the interference method for the measurement of the temperature variation of two of the three principal refractive indices of mica, the thermo-optic behaviour of which has not been investigated before. The results obtained have been discussed with special reference to the theory of thermo-optic behaviour proposed by G. N. Ramachandran (1947) and applied by him with striking success to a large number of transparent solids.

2. Principle of the Method

The usual way of studying the dependence of refraction on temperature is to obtain the refractive indices of a prism of the substance at different temperatures. This is an arduous task in any case, and it is out of the question for substances like diamond and mica where large prisms are not available. The interference method, on the other hand, directly measures the *change* in refractive index caused by a given variation in temperature. Transmitted interference fringes are provided by a thin and fairly uniform plate of the substance, coated on both sides with a reflecting film to enhance the contrast and sharpness of the bands. On heating the crystal, the fringes shift in position, the shift depending on the change in the refractive index as well as the thickness of the substance. If the change in thickness is known, and the fringe shift measured, the change in refractive index can be computed. The method therefore requires a knowledge of the linear expansion of the substance.

The fringes used may be of the Haidinger or Newtonian variety; but in the present investigation the well-known Edser-Butler fringes have been used for the first time in the determination of thermo-optic behaviour. A parallel beam of white light, after traversing the crystal normally, is incident on the slit of a spectrograph. In the field of view of the spectrograph a banded spectrum will be seen, the distance in wave numbers between successive fringes decreasing with decrease in wave-length. Heating the crystal causes a shift in the position of the fringes and by photographing the banded spectra at different temperatures on the same negative, using a Hartmann diaphragm, the fringe shifts for any desired wavelength can be measured. The advantage of this method over using Haidinger or Newtonian fringes is that all wave-lengths are simultaneously recorded in the same picture, the spectrograph serving as a monochromator for each wave-length.

A birefringent crystal will give two sets of banded spectra, owing to the presence of two orthogonally polarised rays having slightly different refractive indices, thus giving rise to a complicated fringe system. But in the case of mica, the axis X of the index ellipsoid (which is the acute bisectrix of the angle between the optic axes) is perpendicular to the cleavage plane. Thus the two rays into which unpolarized light is divided on normally entering the crystal have their directions of vibration *in the plane of the mica.* Their refractive indices are the principal refractive indices n_2 and n_3 in the usual notation. Since their vibration directions are in the plane of the mica, a suitably oriented Nicol placed in front of the crystal will cut off one of the rays completely. There are two positions of the Nicol (at right angles to each other) for which the spectrum will consist of only one set of bands. This is to be expected since the directions of vibration of the two rays are at right angles. The banded spectrum corresponding to a particular ray could be identified from the separation of the bands. It will be shown later that the separation between the bands (in wave-lengths) is inversely proportional to the refractive index of the ray. Hence, in a given wave-length range, there will be a greater number of bands of the ray with the higher refractive index than of the ray with the lower one.

3. EXPERIMENTAL DETAILS

A sheet of muscovite mica (0·03 mm.) was obtained by cleavage and its thickness accurately measured. The mica was coated on both sides with an aluminium film by the usual evaporation method. The thickness of the films was adjusted so that the transmission coefficient was about twenty per cent. The crystal was then cemented at one end with sodium silicate inside a longitudinal slot cut in a glass rod. The other end of the glass rod slid tightly into a hole in a wooden block which was clamped to a stand loaded down with weights. The same stand carried an electric heater provided with windows for observation. The heater could be slid over the glass rod so that the mica was at the level of the windows. Temperatures were measured with the aid of a thermo-couple kept nearly touching the mica and having a calibrated galvanometer in series.

Light from a hundred-watt lamp with a frosted bulb, restricted by means of suitable apertures, was focussed on to the slit of a Fuess spectrograph by means of a long focus lens in the 2*f*-2*f* position, the convergence of the beam being very small. The mica was placed normally in the path of the beam before it entered the spectrograph. A Nicol placed with its axis perpendicular to the mica served to cut out one ray. Using a Hartmann diaphragm, photographs of the banded spectrum were obtained on the same negative first at room temperature and then at a steady temperature of 180°C. A spectrum of the iron arc was also taken on the same negative, using the Hartmann diaphragm, to indicate the wave-length at different regions. A typical photograph is reproduced in Fig. 1. Photographs were taken with panchromatic plates for the red-green region and selochrome plates for the green-blue region. The Nicol was then rotated through 90° to obtain the other ray and photographs taken in a similar manner.

FIG. 1

Photograph of the bands from λ 4400 to λ 6400, showing
(*a*) bands at room temperature
(*b*) bands at about 180° C.
(*c*) iron arc spectrum

To identify the refractive indices along the principal vibration directions of the mica, photographs of the two band systems at room temperature were taken one below the other on the same negative, using the Hartmann diaphragm. The number of bands in one system corresponding to 10 bands in the other was carefully measured and hence the orientation of the Nicol corresponding to the smaller refractive index n_1 and the greater index n_2 ascertained.

The measurements of the band-widths at different wave-lengths were carried out with the aid of a Hilger cross-slide micrometer. On heating the crystal, each fringe was found to have shifted to a slightly longer wavelength. By taking photographs at a few intermediate temperatures, it was ascertained that the shift for a temperature change of 145° was much less than a band-width. The fringe shift was measured as a fraction of the band-width in that region, the mean wave-length of the region being measured from the spectrum of the iron arc.

4. RESULTS

The calculation of results can be carried out in the following manner. The bright bands satisfy the relation

$$2\mu l = N\lambda, \tag{1}$$

where μ is the refractive index and l the thickness of the crystal. N, the number of waves in the crystal decreases in steps of unity as we proceed, band by band towards longer wave-lengths. Thus, if we take the next bright band at the higher wave-length $(\lambda + \lambda_m)$, we can write

$$2\mu l = (N - 1)(\lambda + \lambda_m) \tag{2}$$

the dispersion of the mica over this range of wave-length being negligible.

From (1) and (2) we get

$$N\lambda_m = \lambda + \lambda_m \simeq \lambda$$

$$\text{or} \quad \lambda_m = \frac{\lambda}{N} = \frac{\lambda^2}{2\mu l} \tag{3}$$

which shows that the band-widths for the two rays are inversely proportional to their refractive indices.

If, on heating the crystal by Δt° C., the band of chromatic order N shifts by a wave-length $\Delta\lambda$, we have, on differentiating (1)

$$\left(2\frac{d\mu}{dt}l + 2\mu\frac{dl}{dt}\right)\Delta t = N\,\Delta\,\lambda$$

$$\text{or} \quad \frac{d\mu}{dt} = \frac{N}{2l}\frac{\Delta\lambda}{\Delta t} - \frac{\mu}{l}\frac{dl}{dt} = \frac{N}{2l}\frac{\Delta\lambda}{\Delta t} - \mu a \tag{4}$$

$$\text{Since} \quad \frac{1}{l}\frac{dl}{dt} = a \tag{5}$$

where a is the linear expansion perpendicular to the cleavage plane.

We have determined $\Delta\lambda$ as a fraction of the band-width, *i.e.*,

$$\Delta\lambda = \Delta N \cdot \lambda_m \text{ (say)}$$

$$= \Delta N \cdot \frac{\lambda}{N} \qquad \text{from (3)}$$

$$\text{Thus, from (4),} \quad \frac{d\mu}{dt} = \frac{\lambda}{2l}\frac{\Delta N}{\Delta t} - \mu a. \tag{6}$$

The thickness l can be accurately measured and knowing α, $\frac{d\mu}{dt}$ can be evaluated for the indices n_2 and n_3. α has been recently measured by Hidnert and Dickson (1945). While the average value for muscovite mica seems to be about 17×10^{-6}, individual samples show enormous variations in expansion, especially at high temperatures. For this reason, measurements of thermo-optic behaviour at higher temperatures have not been made in this investigation. Even in the determinations made at low temperatures, there may be an error in the value of α assumed here, so that the absolute values of $\frac{d\mu}{dt}$ may not be correct. But the error is only a constant one and will not affect the *course* of the curve of $\frac{d\mu}{dt}$ against λ, which is the focus of theoretical interest.

The data are reproduced in Table I and plotted graphically in Fig. 2.

TABLE I

Wavelength Å.U.	$-10^6 \frac{dn_2}{dt}$	Wavelength Å.U.	$-10^6 \frac{dn_3}{dt}$
4330	4·40	4320	3·77
4530	5·20	4512	4·55
4790	6·14	4790	4·94
5050	6·41	5060	5·40
5250	6·70	5260	5·87
5587	7·45	5590	6·10
6100	7·75	6100	6·32
6380	7·94	6350	6·84

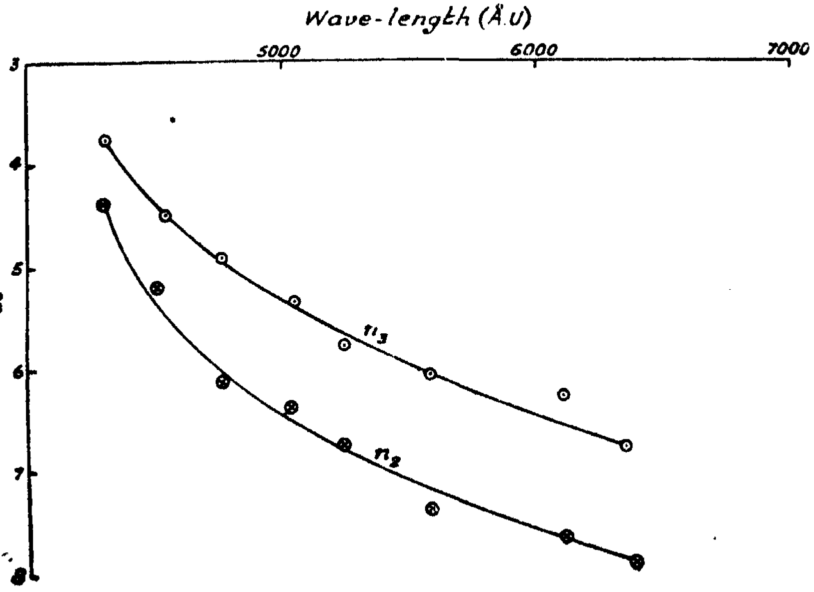

FIG. 2

5. DISCUSSION

The thermo-optic behaviour of a solid and the course of the curve of $\frac{d\mu}{dt}$ against λ can be discussed most fruitfully from the standpoint of a theory proposed by G. N. Ramachandran (1947). He shows that the change in refractive index can be regarded as a superposition of two effects. The first effect is a *decrease* in refractive index with increasing temperature, caused by the decrease in density and hence the number of oscillators in unit volume. The second effect arises from the shift of the absorption frequencies of the solid which are responsible for its dispersion. This shift is in general towards *higher* wave-lengths for absorption frequencies in the nearer ultra-violet and hence tends to *increase* the refractive index. For our purpose, it is sufficient to lump all ultra-violet frequencies into a single term, while contributions from infra-red absorptions are negligible.

The first effect is negative and independent of the wave-length of the light, but the second effect is positive and proportional to a term of the type

$$\frac{1}{(\nu_0^2 - \nu^2)^2}$$

where ν_0 is the ultra-violet absorption frequency. The magnitude of this increases rapidly with decreasing wave-length.

Superposing the two effects, we find that at long wave-lengths the second term is small so that $\frac{d\mu}{dt}$ is large and negative. As the wave-length decreases, however, the second term rapidly becomes larger so that $\frac{d\mu}{dt}$ becomes less and less negative at a steeply rising rate. This is just what is observed in the two curves. The behaviour of mica is typical of that of many other substances like quartz, for instance. In the case of quartz, studies have been extended to the remote ultra-violet and show that the second effect becomes so powerful as to make the temperature coefficients zero and then positive.

The behaviour of the two rays is similar, showing that the second term is characterized by the same absorption frequency in both, but with different oscillator strengths. This is just what is to be expected. It is apparently anomalous that the ray having the larger index should have a smaller temperature coefficient, but an explanation is at once forthcoming when we remember that a smaller negative coefficient implies a larger *positive* contribution from the ultra-violet absorption frequency caused by the higher oscillator strength which goes with the larger index.

Thus all the experimental features can be qualitatively explained on the basis of Ramachandran's theory. A quantitative explanation is not possible without the knowledge of the dispersion, birefringence and ultra-violet characteristic frequencies of muscovite.

I wish to express my gratitude to Prof. R. S. Krishnan for his guidance during this investigation.

SUMMARY

The temperature variation of two of the refractive indices of muscovite mica has been determined by an interference method which can be utilised for other solids as well. The experimental values have been discussed theoretically and shown to conform to the general behaviour of transparent solids as given by Ramachandran's thermo-optic theory.

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THE DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part V. The Fluorspar Structure

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1. INTRODUCTION

RECENTLY a rigorous method was developed (Ramanathan, 1947) for the calculation of the frequencies of the various modes of vibration of a crystal in terms of a general set of force constants, based on the theory of crystal dynamics first put forward by Sir C. V. Raman (1943). The method which is applicable to all crystals was used there to calculate the frequencies of the normal modes of vibration of several cubic structures like that of the diamond, rocksalt, cæsium chloride and the face-centred and body-centred cubic lattices. The success of the method in satisfactorily explaining the experimental results obtained with various crystals (Raman, *et al.*, 1947) encourages us to proceed further and apply it also to crystals for which much experimental data is not available. We shall here consider the fluorspar structure which is typical of a number of crystals.

2. THE FORCE CONSTANTS

The structure of fluorspar consists of three interpenetrating face-centred cubic lattices, two of which are of fluorine and the third of calcium. Considering a unit cube of calcium atoms, the fluorines are situated at the body centres of the eight small cubes formed by joining the midpoints of the edges of the unit cube. In such a structure every calcium atom is surrounded by eight fluorines and every fluorine by four calciums. The nearest neighbours of any atom are always situated along the trigonal directions of the cube. The twelve next-nearest neighbours of every calcium atom are also calciums situated at the midpoints of the twelve edges of a cube of twice the linear dimensions as that of the unit cube, with the atom under consideration at its centre. The six next nearest neighbours of every fluorine and its twelve neighbours next to it are also fluorines, the former situated at the six face-centres and the latter at the midpoints of the twelve cube edges of a unit cube described with the atom under consideration at the body centre.

In the following calculation the forces acting on every calcium atom due to its own displacement and the displacements of the 20 atoms nearest to it are considered as also the forces acting on every fluorine atom due to its own displacement and the displacements of the 22 nearest atoms surrounding it. The total number of force-components 384, $(3 + 9 \times 20 + 3 + 9 \times 22)$ are reduced to 14 independent force-constants by applying the principles of symmetry already described in the work referred to above. The 14 force-constants thus obtained are described in Tables I and II.

TABLE I

Description of the forces acting on any calcium atom due to its own displacement and due to the displacements of its 20 nearest neighbours

Atoms responsible for the forces	Symbol	Description of Force Constants
0	P_1	Force on any calcium atom proportional to its own displacement
1 to 8 (Fluorines)	Q	Direction of both force and displacement along any one of the three cube axes
,,	R	Direction of displacement along a cube axis and that of force along any one of the other two cube axes
9 to 20 Calciums	S_1	Both force and displacement in a direction perpendicular to the cubic plane containing the two atoms
,,	T_1	Direction of both force and displacement along any one of the three cube axes, the plane containing the two being the cubic plane containing the two atoms
,,	U_1	Force and displacement along different cube axes, the plane containing the two being the cubic plane containing the two atoms

TABLE II

Description of the forces acting on any fluorine atom due to its own displacement and the displacements of its 22 nearest neighbours

Atoms responsible for the forces	Symbol	Description of Force Constants
0	P_2	Force on any fluorine atom proportional to its own displacement
1 to 4 (Calciums)	Q R	Described in Table I
5 to 10 (Fluorines)	S_2	Force and displacement perpendicular to the cubic plane containing the two atoms
,,	T_2	Force and displacement parallel to each other and to the line joining the two atoms
11 to 22 (Fluorines)	U_2	Force and displacement perpendicular to the cubic plane containing the two atoms
,,	V	Force and displacement along the same cubic axis, the plane containing the two being the cubic plane containing the two atoms
,,	W	Force and displacement along different cube axes, the plane containing the two being the cubic plane containing the two atoms

It is now possible to derive some relations between the force constants by using the fact that a translation of the entire crystal by an infinitesimally small amount involves no work and the fact that the work involved in a translation of all the calcium atoms alone by a very small amount δx will be the same as the work to be done in translating all the fluorine atoms by the same amount, the calcium atoms now remaining at rest. Or

$$\delta x \{(P_1 + 8Q + 4S_1 + 8T_1) + 2(P_2 + 4Q + 4S_2 + 2T_2 + 4U_2 + 8V)\} = 0 \quad (1)$$

and

$$(P_1 + 4S_1 + 8T_1)\,\delta x = 2(P_2 + 4S_2 + 2T_2 + 4U_2 + 8V)\,\delta x \quad (2)$$

Combining (1) and (2) we have

$$(P_1 + 4S_1 + 8T_1) = -8Q = 2(P_2 + 4S_2 + 2T_2 + 4U_2 + 8V). \quad (3)$$

3. THE FREQUENCY EXPRESSIONS

The normal modes of vibration of the structure of fluorspar can be derived from a consideration of the four modes of vibration of a face-centred cubic lattice having one atom per unit cell, *viz.*, the normal and tangential oscillations of the octahedral planes of atoms and the normal and tangential oscillations of the cubic planes of atoms having degeneracies of 4, 8, 3 and 6 respectively. We have here to consider the three possibilities: (i) The Ca and the two F atoms in any unit cell in the same phase of vibration; (ii) The Ca atom in one phase and the two F atoms in the opposite phase; and (iii) the two F atoms move in opposite phases the Ca atom remaining at rest. Therefore corresponding to every distinct mode of the face-centred cubic lattice, we have here three distinct modes. In addition to the 12 modes thus obtained, there will be two more oscillations of the lattice, in one of which the Ca lattice oscillates against the two F lattices while in the other, the two F lattices oscillate against each other, the Ca lattice remaining at rest. A description of the fourteen modes is contained in Columns 2 and 3 of Table III. Expressions for the frequencies of vibration of the fourteen modes obtained in terms of the force-constants described in Tables I and II are also contained in Table III. As the method of arriving at the frequency expressions is already described fully in the earlier work referred to above, details are not given here.

TABLE III

Expressions for the Frequencies of the fourteen normal modes of fluorspar structure

Degeneracy	Oscillating Units	Direction of oscillation	Expressions for the frequencies $4\pi^2c^2\nu^2$
3	Ca lattice against the F lattices	Arbitrary	$\left(\frac{8Q}{m_1}+\frac{4Q}{m_2}\right)=\left[\frac{P_1+4S_1+8T_1}{m_1}+\frac{P_2+4S_2+2T_2+4U_2+8V}{m_2}\right]$
3	The two F lattices against each other	do	$(P_2-4S_2-2T_2+4U_2+8V)/m_2$
4	(111) planes	[111]	$\frac{P_1-8U_1}{2m_1}+\frac{P_2-8W}{2m_2}\pm\left\{\left[\frac{P_1-8U_1}{2m_1}-\frac{P_2-8W}{2m_2}\right]^2+\frac{2(2Q-4R)^2}{m_1m_2}\right\}^{\frac{1}{2}}$
4	(111) do	[111]	
4	(111) do	[111]	$(P_2-8W)/m_2$
8	(111) do	Tangential	$\frac{P_1+4U_1}{2m_1}+\frac{P_2+4W}{2m_2}\pm\left\{\left[\frac{P_1+4U_1}{2m_1}-\frac{P_2+4W}{2m_2}\right]^2+\frac{2(2Q+2R)^2}{m_1m_2}\right\}^{\frac{1}{2}}$
8	(111) do	do	
8	(111) do	do	$(P_2+4W)/m_2$
3	(100) do	[100]	$(P_1+4S_1-8T_1)/m_1$
3	(100) do	[100]	$(P_2+4S_2-2T_2+4U_2-8V)/m_2$
3	(100) do	[100]	$(P_2+4S_2+4U_2)/m_2$
6	(100) do	Tangential	$(P_1-4S_1)/m_1$
6	(100) do	do	$(P_2+2T_2-4U_2)/m_2$
6	(100) do	do	$(P_2+2S_2+2T_2+4V)/m_2$

4. SOME FURTHER SIMPLIFICATIONS

The twelve constants appearing in the frequency formulæ of Table III are connected by the two relations (3). It is possible to simplify the formulæ further by making some justifiable assumptions, *viz.*, that those forces in which the directions of both force and displacement are perpendicular to the cubic plane containing the two atoms are of negligible magnitude. We can thus eliminate the constants S_1, S_2 and U_2. Further, if the forces are strictly central, then $Q = R$, $T_1 = U_1$ and $V = W$. Even if the force field deviates slightly from central forces, the above relations hold as a good approximation to the real state of affairs. We thus have the fourteen frequencies expressed in terms of five constants connected by the relation.

$$(P_1 + 8T_1) = -8Q = 2(P_2 + 2T_2 + 8V) \qquad (4)$$

The simplified formulæ are contained in Column 4 of Table IV.

TABLE IV

Simplified Expressions for the fourteen modes of vibration using 5 constants

Degeneracy	Oscillating units	Direction of oscillation	Frequency expressions $4\pi^2c^2\nu^2$
3	Ca and F lattices	Arbitrary	$\left\{\frac{P_1+8T_1}{m_1}+\frac{P_2+2T_2+8V}{m_2}\right\}=-\left\{\frac{8Q}{m_1}+\frac{4Q}{m_2}\right\}$
3	F lattices	do	$(P_2-2T_2+8V)/m_2$
4	(111) planes	Normal	$\left(\frac{\frac{7}{8}P_1-3T_1}{m_1}\right)+\left(\frac{\frac{1}{4}P_2-3V+\frac{1}{4}T_2}{m_2}\right)$
4	do	do	$\left(\frac{\frac{1}{8}P_1-5T_1}{m_1}\right)+\left(\frac{\frac{1}{4}P_2-5V-\frac{1}{4}T_2}{m_2}\right)$
4	do	do	$(P_2-8V)/m_2$
8	do	Tangential	$\left(\frac{P_1+6T_1}{m_1}\right)+\left(\frac{P_2+T_2+6V}{m_2}\right)$
8	do	do	$-\left\{\frac{2T_1}{m_1}+\frac{2V+T_2}{m_2}\right\}$
8	do	do	$(P_2+4V)/m_2$
3	(100) planes	Normal	$(P_1-8T_1)/m_1$
3	do	do	$(P_2-2T_2-8V)/m_2$
3	do	do	P_2/m_2
6	do	Tangential	P_1/m_1
6	do	do	$(P_2+2T_2)/m_2$
6	do	do	$(P_2+2T_2+4V)/m_2$

SUMMARY

Exact expressions for the frequencies of the fourteen normal modes of the fluorspar structure are derived in terms of 12 force constants which take account of the influence of the 20 nearest neighbours of each calcium atom and 22 nearest neighbours of each fluorine atom. Simplified formulæ are also given which involve only five constants connected by an additional relation.

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DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part VI. The Zinc Sulphide Structure

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1. INTRODUCTION

THE zinc sulphide structure is typical of many crystals and therefore expressions for the frequencies of its eigenvibrations are derived in what follows by using the method described in Part I of this series (Ramanathan, 1947).

2. THE FORCE CONSTANTS

As is well known, the structure of this crystal is similar to that of diamond and consists of two interpenetrating face-centred cubic lattices of zinc and sulphur atoms. Each zinc and sulphur atom in the structure has as its nearest neighbours, four atoms of the other kind situated along trigonal directions of the crystal. The next nearest neighbours of any atom are twelve atoms of the same kind situated at the midpoints of the twelve edges of a unit cube described with the atom under consideration at its centre. The $294 [= 2(3 + 16 \times 9)]$ force-components arising out of a consideration of the influence of the 16 atoms surrounding every atom in the crystal can be reduced by applying the principles of symmetry, to 14 force-constants of which only 10 appear in the frequency formulæ, as will be seen later. A description of these 10 constants is contained in Table I below.

The fact that a translation of the entire crystal by an infinitesimally small amount δx involves no restoring forces, leads us to the two relations:

$$P_1 + 4Q + 4S_1 + 8U_1 = 0 \tag{1}$$

$$P_2 + 4Q + 4S_2 + 8U_2 = 0 \tag{2}$$

Or

$$(P_1 + 4S_1 + 8U_1) = -4Q = (P_2 + 4S_2 + 8U_2) \tag{3}$$

TABLE I

Description of the force-constants appearing in the frequency formulæ

*Atoms responsible for the forces	Symbol	Description of the Constants
0	P_1, P_2	Force on any atom proportional to its own displacement along any one of the three cube axes
1 to 4	Q	Direction of both force and displacement along any one of the three cube axes
do	R	Direction of both force and displacement along any two different cube axes
5 to 16	S_1, S_2	Direction of both force and displacement along the same cube axis which is also perpendicular to the cubic plane containing the two atoms
do	U_1, U_2	Both force and displacement along any one of the three cube axes contained in the cubic plane containing the two atoms
do	W_1, W_2	Force and displacement along different cube axes, the directions of the two being contained in the cubic plane containing the two atoms

* Atom 0 may refer to either zinc or sulphur and the other numbers accordingly. The symbols P_1, S_1, U_1 and W_1 refer to zinc atoms, P_2, S_2, U_2 and W_2 to sulphur atoms and Q and R to both.

3. THE FREQUENCY FORMULAE

As in the case of diamond, the normal modes of the zinc sulphide structure can also be derived from a consideration of the four modes of a face-centred cubic lattice, *viz.*, the normal and tangential oscillations of the octahedral planes and the normal and tangential oscillations of the cubic planes,

TABLE II

Showing the complete expressions for the frequencies of the nine normal modes of vibration of the zinc sulphide structure

Degeneracy	Oscillating units	Direction of oscillation	*Expressions for the frequencies $4\pi^2c^2\nu^2$
3	The two lattices	Arbitrary	$(P_1+4S_1+8U_1)/\mu = (P_2+4S_2+8U_2)/\mu = -\frac{4Q}{\mu}$
4	(111) planes	Normal	$\frac{P_1-8W_1}{2m_1}+\frac{P_2-8W_2}{2m_2}\pm\left\{\left[\frac{P_1-8W_1}{2m_1}-\frac{P_2-8W_2}{2m_2}\right]^2+\frac{(2Q-4R)^2}{m_1m_2}\right\}^{1/2}$
4	do	do	
8	do	Tangential	$\frac{P_1+4W_1}{2m_1}+\frac{P_2+4W_2}{2m_2}\pm\left\{\left[\frac{P_1+4W_1}{2m_1}-\frac{P_2+4W_2}{2m_2}\right]^2+\frac{(2Q+2R)^2}{m_1m_2}\right\}^{1/2}$
8	do	do	
3	(100) planes	Normal	$(P_1+4S_1-8U_1)/m_1$
3	do	do	$(P_2+4S_2-8U_2)/m_2$
6	do	Tangential	$\frac{P_1-4S_1}{2m_1}+\frac{P_2-4S_2}{2m_2}\pm\left\{\left[\frac{P_1-4S_1}{2m_1}-\frac{P_2-4S_2}{2m_2}\right]^2+\frac{16R^2}{m_1m_2}\right\}^{1/2}$
6	do	do	

* m_1 refers to the mass of the zinc atom, m_2 to the mass of the sulphur atom and μ to the reduced mass given by $\left(\frac{1}{\mu}=\frac{1}{m_1}+\frac{1}{m_2}\right)$.

the phase of the vibration being reversed at each successive equivalent layer of atoms. Since there are two non-equivalent atoms per unit cell in the present case, there will be two possibilities corresponding to every one of the above four. Finally there will be one more vibration, which is the oscillation of the zinc and sulphur lattices against each other along any three orthogonal directions. All the nine modes of vibration are described in Columns 2 and 3 of Table II. Column 4 of Table II contains the expressions for the frequencies of the nine normal modes derived in terms of the 10 constants described in Table I.

4. SOME FURTHER SIMPLIFICATIONS

The quantities S_1 and S_2 are bound to be negligible because they are forces in which the directions of both force and displacement are perpendicular to the cubic plane containing the two interacting atoms and consequently involve no change in their distance. We can further put $U_1 = W_1$ and $U_2 = W_2$, under the assumption that the forces are along the line joining the two atoms for the more distant neighbours. Thus, we are left with the constants P_1, P_2, Q, R, U_1 and U_2 connected by the relation

$$(P_1 + 8U_1) = (P_2 + 8U_2) = -4Q. \tag{4}$$

TABLE III

Showing simplified expressions for the frequencies of the various modes of vibration

Degeneracy	Oscillating units	Direction of oscillation	Simplified Expressions $4\pi^2 c^2 \nu^2$
3	The two lattices	Arbitrary	$\frac{P_1+8U_1}{m_1} + \frac{P_2+8U_2}{m_2} = -\frac{4Q}{\mu}$
4	(111) Planes	Normal	$\frac{P_1-8U_1}{m_1} + \frac{P_2-8U_2}{m_2} - \frac{(P_1-8U_1)(P_2-8U_2)-(2Q-4R)^2}{(P_1-8U_1)m_2+(P_2-8U_2)m_1}$
4	do	do	$\frac{(P_1-8U_1)(P_2-8U_2)-(2Q-4R)^2}{(P_1-8U_1)m_2+(P_2-8U_2)m_1}$
8	do	Tangential	$\frac{P_1+4U_1}{m_1} + \frac{P_2+4U_2}{m_2} - \frac{(P_1+4U_1)(P_2+4U_2)-(2Q+2R)^2}{(P_1+4U_1)m_2+(P_2+4U_2)m_1}$
8	do	do	$\frac{(P_1+4U_1)(P_2+4U_2)-(2Q+2R)^2}{(P_1+4U_1)m_2+(P_2+4U_2)m_1}$
3	(100) Planes	Normal	$\frac{(P_1-8U_1)}{m_1}$
3	do	do	$\frac{(P_2-8U_2)}{m_2}$
6	do	Tangential	$\frac{P_1}{m_1} + \frac{P_2}{m_2} - \frac{P_1P_2-16R^2}{P_1m_2+P_2m_1}$
6	do	do	$\frac{P_1P_2-16R^2}{P_1m_2+P_2m_1}$

Also, since by the nature of the forces $P_1 \gg U_1$ and $P_2 \gg U_2$ and further U_1 and U_2 are of the same sign, it follows that $P_1 \approx P_2$. Under these simplifying assumptions the frequencies of the nine normal modes can be expressed as shown in Table III in terms of six independent constants connected by two additional relations (4).

SUMMARY

Expressions for the frequencies of the nine normal modes of the zinc sulphide structure are derived in terms of 10 force-constants taking account of the interaction of each atom with its 16 nearest neighbours. The formulæ, after simplification contain only six constants which are further connected by two additional relations.

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PHOTOMETRY OF RAMAN SPECTRA OF CRYSTALS

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1. Introduction

Owing to the extreme feebleness with which many of the Raman lines are recorded even after long exposures, an accurate determination of their intensities, absolute as well as relative is beset with many difficulties. Also it is well known that the data available on the subject are so inconsistent and contradictory that it is not possible to come to any definite conclusions regarding the validity of the existing theory of Raman effect in its entirety. The observations concerning the variation of the intensity of Raman lines in carbon tetrachloride by K. S. Krishnan, (1929), R. Anantha Krishnan (1938) and Sirkar (1943) showed that the intensity of the Stokes line did not increase with temperature. Brickwedde and Peters (1929) concluded from a study of the temperature variations of the Raman effect in quartz that the Stokes lines became weaker at higher temperatures. Landsberg and Mandelstamm (1930) reinvestigated the problem in the case of crystalline quartz and reported an increase of intensity for the Stokes component of the Raman line at 465 cm.$^{-1}$ in the ratio 1 : 1·29 when the temperature was raised from 295° to 810° T. Although the expected increase was in the ratio 1 : 1·6 they concluded that the deviation was well within the limits of accuracy attainable in the measurement. More recent work by Ornstein and Went (1935) and K. Venkateswarlu on a few crystals including calcite and quartz confirms the observations of the earlier workers. The general inferences of all these workers are that : (1) the ratio of the intensity of the Stokes and the anti-Stokes lines are in fair agreement with the theoretically calculated values; (2) the absolute intensity of the Stokes lines showed a marked decrease with rise of temperature; (3) the intensity of the anti-Stokes lines increased with rise of temperature but far slower than predicted by theory (except in the case of calcite); and (4) the deviations are most pronounced in the case of low frequency shift lines.

2. Theoretical

On the basis of Placzek's theory of Raman effect, the aggregate intensities of the Stokes and the anti-Stokes Raman lines are given by

$$I_{(\nu-\nu_j)} = \frac{64\pi^4}{3c^3}\{4A_{1j}^2 - 7B_{1j}^2\}(\nu-\nu_j)^4 \frac{1}{1-e^{-\frac{h\nu_j}{kT}}}$$

and

$$I_{(\nu+\nu_j)} = \frac{64\pi^4}{3c^3}\{4A_{1j}^2 - 7B_{1j}^2\}(\nu+\nu_j)^4 \frac{1}{e^{\frac{k\nu_j}{kT}}-1},$$

where A_{1j} and B_{1j} are the invariants of the symmetric tensor $\left(\frac{\partial\alpha}{\partial q_j}\right)_0$. The ratio of the intensity of the Stokes Raman line to that of the corresponding anti-Stokes line is given by

$$\frac{I_{(\nu-\nu_j)}}{I_{(\nu+\nu_j)}} = \left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 e^{\frac{k\nu_j}{kT}}.$$

It is evident that the experimental results regarding the individual intensities are in sharp disagreement with the values calculated from formulæ (1) and (2). R. Ananthakrishnan (1938) pointed out that the effect of anharmonicity is not explicitly taken into account in Placzek's theory. $\left(\frac{\partial\alpha}{\partial q_j}\right)_0$ which determines the intensity of the Raman line cannot be assumed to be independent of the internuclear distances; on the contrary it decreases with increasing nuclear separation. K. Venkateswaralu (1947) showed that by assuming $\left(\frac{\partial\alpha}{\partial q_j}\right)_0$ to be a function of the amplitude of vibration, the experimental results could be satisfactorily explained. As the contribution to the intensity of the Raman lines from transitions involving higher quantum numbers become more and more important with increasing temperature, in the case of low frequency shifts, the effect of the increased amplitude of vibration on the change in polarisability cannot be neglected.

However, the ratio of the Stokes to the anti-Stokes intensity can be expected to be in agreement with expression (3) as the factor involving $\left(\frac{\partial\alpha}{\partial q_j}\right)_0$ is absent and the experiments of K. Venkateswaralu (1942, 1943) have shown that the ratio of the Stokes to the anti-Stokes lines is in better agreement with the modified formula than the classical Boltzmann formula alone on the basis of which the earlier workers interpreted their results. As only low frequency shift lines have been measured so far, the difference between the two does not amount to more than 10% and is quite within the limits of experimental error. The question can be taken to be settled beyond a doubt only when the intensity ratio has been measured for a few high frequency shift lines where the factor $\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4$ will differ considerably from unity. With the help of a new technique, a detailed investigation has therefore been undertaken by the author.

3. EXPERIMENTAL TECHNIQUE

The chief difficulty experienced by the earlier investigators was their inability to record the anti-Stokes lines of faint Raman lines, as also those with frequency shifts greater than 480 cm.$^{-1}$, the exciting radiation being λ 4047 or λ 4358 of mercury. But the ultra-violet technique developed and perfected by R. S. Krishnan in this laboratory may with decided advantage be used instead and the enormously increased scattering power of the resonance radiation arising from its exceptional intensity as compared with the other mercury radiations and from the λ^{-4} law make it possible to record the anti-Stokes lines of even very faint Raman lines. Further, as the λ 2536·5 Å.U. radiation from the light scattered by the medium is effectively suppressed by absorption in a long column of mercury vapour, the Raman lines are obtained on a clear background and no correction need be made for the continuous background.

Another obstacle in the way of an accurate measurement of the relative intensity of the Stokes and anti-Stokes components for frequency shifts greater than 350 cm.$^{-1}$ is the great disparity in their intensities so that a direct comparison of the lines on one and the same plate is unlikely to yield any reliable result. But by taking a series of exposures for the Stokes line of different time intervals a comparison may be made with the intensity of the anti-Stokes line recorded in another exposure. For this a complete knowledge of the characteristics of the photographic plate used is necessary and fluctuations in the intensity of the light source during the exposure will vitiate the result considerably. All these difficulties and errors get automatically eliminated by the use of an ultra-violet Spekker photometer in conjunction with a medium quartz spectrograph. The experimental technique used in this case enables one to determine with a fair accuracy the intensity ratios even in the case of high frequency shift Raman lines. The results obtained with the Spekker in the case of Raman lines of small shifts were checked with the help of the direct method and the values never differed by more than 5%.

The Raman spectra of the crystals investigated were excited by means of the resonance radiation of mercury from a water-cooled magnet controlled quartz arc. The scattered light from the crystal was focussed on the tungsten-steel spark gap of the Spekker photometer with the help of the ivory indicator. The image acted as the source for the Spekker and the light from it was divided into two paths by a suitable arrangement of prisms. Each one contained an aperture, one being fixed and the other one being variable by means of a shutter mechanism operated by a calibrated screw directly giving the value of $\log_{10}\frac{I_0}{I}$, where $\frac{I_0}{I}$ is the ratio of the intensities of the beams passing through the two apertures. The beams were then focussed by means of quartz lenses and the light paths were brought into close juxtaposition on the slit of the quartz spectrograph by means of quartz rhombs. Thus the spectrograph was illumined by two beams of light having the same origin, the intensity of one reduced by a known amount. It becomes now possible to compare the intensity of the Stokes line recorded from the light passing through the reduced aperture with the intensity of the anti-Stokes line recorded with the full aperture. The actual ratio can be calculated from a knowledge of the $\log_{10}\frac{I_0}{I}$ value. No error can occur because of fluctuation in the intensity of the quartz arc. The Spekker photometer though specially designed to work at high density values cannot be relied upon to give intensity ratios over 250 with very great accuracy as in those regions any small error in the photographic estimate will be magnified hundredfold when the actual ratio is calculated.

Ilford Special Rapid plates used throughout this work were calibrated by the method of varying slit-widths with the help of a tungsten lamp provided with a quartz window. A measurement of the ratio of the slopes of the characteristic curves of the photographic plate at 2 or 3 different wavelengths in the neighbourhood of λ 2537 showed that the Schwarzschild constant p was practically constant. Further the work of G. R. Harrison (1925) shows that for about 100 Å.U. on either side of λ 2537 the photographic sensitivity for a similar type of plate remains fairly uniform. As such no attempt was made to draw the characteristic curves at wavelengths corresponding to the different Raman lines and all the intensities were computed from the characteristic curves drawn for a mean wavelength of λ 2540. The plates were developed in the same stock developer, for the same time and the photographs were restricted to the centre of the plate to avoid any error due to the difference in the rate of development near the edges.

4. RESULTS AND DISCUSSION

A preliminary report of the results that have so far been obtained in the case of quartz, calcite, barytes and ammonium di-hydrogen phosphate has been given below along with the theoretically computed values from the Boltzmann formula alone and also from the modified formula. For the purpose of comparison the values obtained by K. Venkateswaralu in the visible region have also been included in the table.

The temperature was taken as 27° C. (room temperature) though as a result of the close proximity of the arc it is quite possible for the temperature of the crystal to have been a few degrees higher in spite of the efficient fan cooling.

Quartz

$$A = e^{\frac{h\nu_j}{kT}} \qquad B = \left(\frac{\nu - \nu_j}{\nu + \nu_j}\right)^4 \qquad C = e^{\frac{h\nu_j}{kT}}\left(\frac{\nu - \nu_j}{\nu + \nu_j}\right)^4$$

ν cm.$^{-1}$	A	B	C	Expl. value	A	C	Expl. value
127	1·834	·9745	1·79	1·78	..	..	..
207	2·687	·9594	2·58	2·43	..	..	..
267	3·58	·9471	3·4	3·2	..	..	..
358	5·53	·9298	5·14	4·95	..	..	..
400	6·75	·9221	6·23	6·0	..	..	..
467	9·31	·9095	8·47	7·00	8·72	7·42	7·68

Calcite

ν cm.$^{-1}$	A	B	C	Expl. value	A	C	Expl. value
155·5	2·102	·9683	2·04	2·01	2·07	1·96	2·00
284	3·88	·9436	3·66	3·61	3·73	3·38	3·30

Barytes

ν cm.$^{-1}$	A	B	C	Experimental value
64	1·36	·9872	1·34	1·53
73·6	1·42	·9854	1·4	1·7
88·3	1·525	·9817	1·5	1·75
127·4	1·84	·9745	1·79	1·83
150·0	2·05	·9701	1·99	1·98
189·0	2·467	·962	2·37	2·45
462·2	9·09	·9103	8·27	10·0

Ammonium di-hydrogen phosphate

ν cm.$^{-1}$	A	B	C	Experimental value
172	2·27	·9656	2·2	2·36

The values obtained for the 465 cm.$^{-1}$ line of quartz and 462·2 cm.$^{-1}$ line of barytes deviate considerably from the theoretical values and the author is at present unable to say if they are genuine. The Spekker photometer has not yet been calibrated with any standard source and the reading on the drum has been taken to represent the correct value. In the case of barytes most of the low frequency Raman lines are doublets and as the intensity ratios have been determined only for the peak intensities, they are bound to be less accurate than in the case of sharp lines like those of calcite. Yet it is obvious that the results are in good agreement with those obtained from the modified formula.

Even after long exposures of the order of a week, the anti-Stokes line of 1158 cm.$^{-1}$ (quartz) was not recorded. This is not surprising in view of the fact that in R. S. Krishnan's spectrogram of the Raman spectrum of quartz (1945) even after the second order lines have made their appearance with considerable intensity the anti-Stokes of 1158 cm.$^{-1}$ is absent.

In conclusion, the author's respectful thanks are due to Prof. R. S. Krishnan for his kind interest and suggestions in the course of this work.

SUMMARY

Using the ultra-violet Spekker photometer and the resonance radiation of mercury as exciter the relative intensities of the Stokes and anti-Stokes Raman lines in the case of calcite, quartz, barytes and ammonium di-hydrogen phosphate have been measured. It is found that the results obtained confirm the theoretical relation that the intensity is proportional to the fourth power of the emission frequency. The new method outlined in this paper makes it possible to measure the intensity ratios in case of high frequency shift Raman lines.

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RAMAN SPECTRUM OF AMMONIUM DI-HYDROGEN PHOSPHATE

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1. Introduction

Ammonium di-hydrogen phosphate ($NH_4H_2PO_4$) has in recent years been subjected to many investigations to elucidate the origin and cause of the Seignette electric anomaly that exists in the case of crystals isomorphic with Rochelle salt and the phosphates and arsenates of the tetragonal class. The elastic, piezo-electric and dielectric constants show analogous variations within the range of stress and temperature in which measurements have so far been carried out (Mason, 1946). Stephenson and Zettlemoyer (1944) noticed a transition point in the specific heat curve at 147·9° K, while Klug and Johnson (1937) and later Jean Jaffray (1944) claim to have observed a second order transformation of the ammonia type at about 19° C. In view of the importance of the subject and as a study of the Raman spectrum of ammonium di-hydrogen phosphate in the form of single crystals can yield valuable information concerning the structure as well as the interatomic forces, an investigation of its Raman spectrum using λ 2536·5 radiation of mercury as exciter, has been undertaken.

The earlier investigations on the Raman spectra of the acids of phosphorus and their salts are not very numerous and the results obtained are very meagre. The solutions of the primary phosphates have been studied by C. S. Venkateswaran (1936) and in the case of $NH_4H_2PO_4$ 30% solution, only 4 lines with frequency shifts 360, 515, 885 and 1090 cm.$^{-1}$, corresponding to the internal oscillations of the PO_4 group, have been reported. The chief difficulty experienced by the earlier workers in recording the Raman spectra of the phosphates is the strong continuous spectrum which appears on every plate obliterating all the faint lines. C. S. Venkateswaran attributed this to the mercury arc itself and by a proper design of the arc and by the use of fan cooling directed towards the cathode, he reduced this to a minimum. However, as C. S. Venkateswaran himself has remarked in his paper, with crystals of the primary phosphates of sodium, potassium and ammonium, he was unable to get any satisfactory picture even after prolonged exposures. Apart from this, no work on $NH_4H_2PO_4$ has so far been reported. The use of the ultraviolet technique removes this difficulty at once as the intense unmodified light is quenched completely from the scattered light before its entry into the spectrograph by a cool mercury vapour filter. This combined with the enormously increased scattering power owing to the use of ultraviolet radiation, made it possible to study the Raman spectrum of ammonium di-hydrogen phosphate.

2. EXPERIMENTAL DETAILS AND RESULTS

Two fine transparent specimens of $NH_4H_2PO_4$ with fully developed faces, one of size 1½ cm. × 1 cm. × ¾ cm. and the other 7″ × 2½″ × 2½″ made in the Bell Telephone Company's laboratories at Murray Hill and presented to Sir C. V. Raman were used in the present investigation, the smaller one being cut suitably to enable a study of the effect of orientation on the Raman spectrum. The spectra were excited by the resonance radiation of mercury from a water-cooled magnet-controlled quartz arc and the scattered light was focussed on to the slit of a Hilger medium quartz spectrograph, all precautions being taken to eliminate parasitic light from fogging the plate.

Fig. 1 (*a*) is a reproduction of the picture obtained with the big crystal and with a slit width of 5 div. (0·025 mm). For this slit width exposures

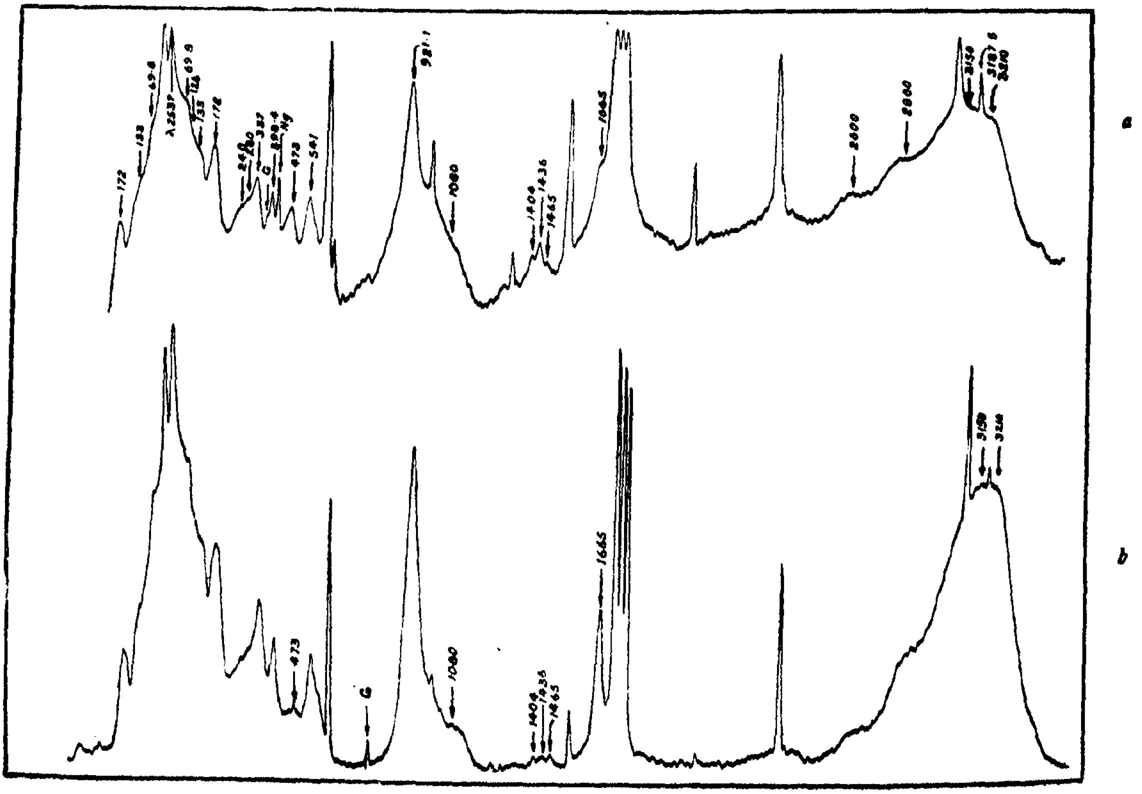

FIG. 2

of the order of 12 hours were found to be necessary to bring out the salient features of the spectrum, while 24 hours were sufficient to get a fairly intense picture. This is a really surprising and noteworthy point, for in the case of the ammonium halides, the exposure times were of the order of 4 hours (R. S. Krishnan, 1947). The characteristic feature of the Raman spectrum of ammonium di-hydrogen phosphate is that all the lines including those due to the internal oscillations of the PO_4 group as well as the NH_4 group are broad though fairly intense.

For a comparative study of the effect of orientation on the Raman spectrum, a picture with the scattered light taken along the tetragonal axis has also been reproduced in Fig. 1 (*c*). Fig 1 (*b*) is the mercury spectrum enlarged to the same extent as the other two. The first spectrogram was recorded with the direction of the scattered light normal to the fourfold axis of symmetry. As is to be expected, the pictures taken with the incident light being respectively along *a* and *b* axes, the direction of the scattered light being along the tetragonal axis, were found to be identical.

The frequency shifts of the Raman lines were evaluated by a comparison with the superposed iron arc spectrum and also by a direct measurement under a Hilger comparator. The Raman shifts of the feeble lines and bands, however, were computed from the microphotometer curves. The frequency shifts and the intensities of the principal Raman lines are listed in **Table I**.

TABLE I

Principal Raman lines of ammonium di-hydrogen phosphate

Serial No.	Group	Frequency shift in $cm.^{-1}$	Nature of the lines
1	lattice	69·8 (4)	very broad
2	do	124 (2)	broad
3	do	133 (2)	..
4	do	172 (4)	broad
5	phosphate	240 (1)	do
6	do	280 (1)	..
7	do	337 (3)	broad and diffuse
8	do	398·4 (2)	sharp
9	do	473 (2)	diffuse
10	do	541 (3)	do
11	do	921·1 (10)	sharp
12	do	1080 (1)	very broad
13	NH_4	1404 (1)	..
14	do	1436 (1)	..
15	do	1465 (1)	..
16	do	1665 (3)	sharp
17	do	2600 (1)	Extremely broad
18	do	2800 (1)	do
19	do	3150 (5)	diffuse
20	do	3210 (5)	..

The Raman lines with frequency shifts 1404, 1435, 1465 and 473 cm.$^{-1}$ were found to be influenced enormously by the direction of scattering and the intensity is considerably greater when the scattered light is taken along the fourfold axis of symmetry.

In the low frequency region the spectrum exhibits two broad bands and one line. The bands extend from 0 to 69·8 cm.$^{-1}$ and from 70 to 133 cm.$^{-1}$ with a sharp cut off at the upper limit. Of these the former is the more intense one. The line at 172 cm.$^{-1}$ is also intense and has a width of about 10 cm.$^{-1}$

3. DISCUSSION

Ammonium di-hydrogen phosphate is isomorphous with KH_2PO_4, KH_2AsO_4 and $NH_4H_2AsO_4$ and crystallises in the tetragonal scalenohedral class. The space group is V_d^{12}. The X-Ray analysis has been carried out by O. Hassel (1920) and he found that the phosphate groups consist of a phosphorus atom tetrahedrally surrounded by four oxygens and that each group is surrounded tetrahedrally by four other groups. Neighbouring PO_4 groups are connected by hydrogen bonds. Like the PO_4 group, the NH_4 group retains its tetrahedral structure. The number of molecules in the unit cell is 4.

From a comparative study of the spectra of the aqueous solutions of the phosphates and the ammonium salts with the frequency shifts observed in the spectrum of $NH_4H_2PO_4$, we may broadly classify the observed lines into three groups, *viz.*, (1) the lattice spectrum, (2) the spectrum of the PO_4 ion and (3) the spectrum of the NH_4 ion. The classification is indicated in Table I.

Lattice spectrum.—The appearance of the two broad bands in the lattice spectrum with continuous distribution of intensity from the exciting line suggests that the ions PO_4 and NH_4 are capable of hindered rotation more or less as in a liquid, the lower frequency band corresponding to the heavier ion. It is quite probable that the bands split up into lines at lower temperatures.

Spectrum of the PO_4 ion.—The PO_4 ion in the free state possesses full cubic symmetry and has only four distinct modes of oscillation with frequency shifts 361 (2), 515 (3), 980 (1) and 1080 (3) cm.$^{-1}$, the figures within brackets giving the degeneracies. In the crystal the PO_4 ion has only the symmetry of the crystal which is lower than that of the free ion. One might therefore expect some of the degeneracies of the characterestic frequencies of the free ion to be removed in the crystal, as indicated in Table II.

TABLE II

Raman frequencies of the PO_4 ion

Nature	$\nu_1(1)$	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
Free state ..	980	363	1082	515
$NH_4H_2PO_4$ ..	921·1	337 ; 358·4	1080	473 ; 541

The splitting of ν_2 and ν_4 into two lines with widely different frequency shifts indicates the strong influence of the hydrogen bond on the PO_4 group. Further investigation has to be carried out before any satisfactory explanation can be given for the presence of the two lines with frequency shifts 240 and 280 cm.$^{-1}$ respectively.

Spectrum of the NH_4 ion.—Because of its tetrahedral symmetry, NH_4 ion in the free state should have only four distinct modes of oscillation of which ν_1 is single, ν_2 is doubly degenerate and ν_3 and ν_4 are triply degenerate. The corresponding Raman shifts are 3033, 1685, 3134 and 1397 cm.$^{-1}$ In the spectra of the ammonium compounds, the most intense line usually corresponds to the totally symmetric oscillation ν_1. Contrary to this, there is no line in the Raman spectrum of $NH_4H_2PO_4$ at room temperature, with a frequency shift 3030 cm.$^{-1}$ It is quite likely that it has shifted to higher frequency and is lost in the intense background due to the Raman lines at 3150 cm.$^{-1}$

TABLE III

Raman frequencies of the NH_4 ion

State	$\nu_1(1)$	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
Free ion ..	3033	1685	3134	1397
NH_4 Br Crystal ..	3027	1686	3121	1398 ; 1429
NH_4Cl Crystal ..	3041	1710 ; 1765	3146	1400 ; 1418 ; 1440
$NH_4H_2PO_4$ ..	..	1665	3150 ; 3210	1404 ; 1437 ; 1465

The partial removal of the degeneracies of the characteristic frequencies of the penta-atomic group in the spectrum of ammonium di-hydrogen phosphate suggests that in the crystal lattice the vibrating NH_4 ion possesses lower symmetry evidently due to the presence of potential fields of the neighbouring ions, although the NH_4 ion has full tetrahedral symmetry when the atoms are at rest.

As in the spectra of the ammonium halides, there are two extra bands, one at 2600 cm.$^{-1}$ and the other at 2800 cm.$^{-1}$ In the case of $NH_4H_2PO_4$ the band with a shift 2600 cm.$^{-1}$ might be due to P–H oscillation. The origin of the other band is at present not clear.

In conclusion, the author wishes to express his grateful thanks to Prof. R. S. Krishnan for his kind interest and valuable suggestions in the course of the work.

SUMMARY

Using the λ 2536·5 mercury resonance radiation as exciter, the Raman spectrum of ammonium di-hydrogen phosphate has been investigated. The spectrum consists of 20 lines of which (1) 4 are lattice lines, (2) 8 are due to internal oscillations of the PO_4 group and (3) 8 due to NH_4 groups. The continuous distribution of intensity in the lattice spectrum indicates the possibility of the existence of hindered rotation of the NH_4 and PO_4 groups. The splitting up of some of the degenerate lines of both PO_4 and NH_4 groups might be due to the strong influence of the hydrogen bonds.

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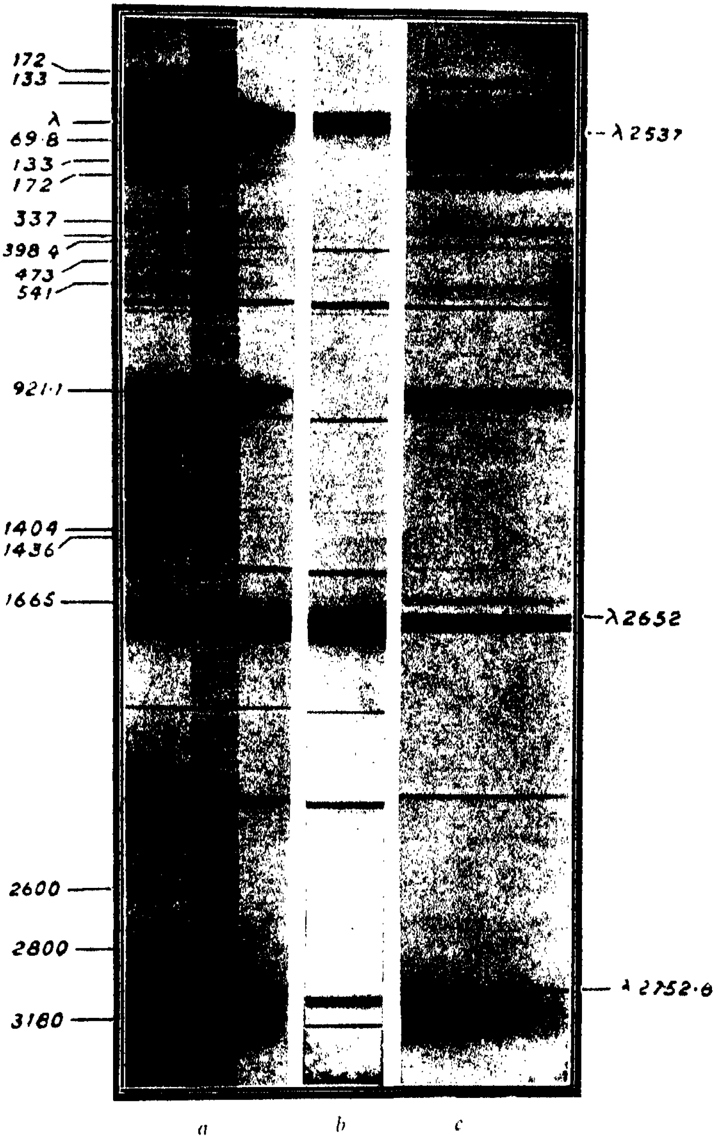
172
133
λ
69·8
133
172
337
398 4
473
541
921·1
1404
1436
1665
2600
2800
3180
λ 2537
λ 2652
λ 2752·6
a
b
c

FIG. 1

A MODIFIED METHOD FOR THE DETERMINATION OF ELASTIC CONSTANTS OF CRYSTALS

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1. Introduction

By exciting a piezo-electric wedge, Bhagavantam and Bhimasenachar[1] obtained a continuous range of ultrasonic frequencies. The elastic constants of several crystalline substances, available only in small sizes, have been successfully determined using such wedges.

It has been found, however, that a wedge often contains a number of discrete frequencies for which the amplitude of piezo-vibration is high. These frequencies are superposed on the continuous spectrum. When a crystal plate is driven by such a wedge, in addition to the natural frequencies of the plate, the wedge maxima force themselves through, giving spurious indications, especially when the frequency is in the region of the lower harmonics of the plate. Analysis of the data in such cases becomes a little difficult, unless the higher harmonics of the plate are excited, when the spurious maxima become few. Efforts have been made recently in this laboratory to get at a wedge without spurious maxima, by working with different shapes and sizes, and considerable success has been achieved. These results will be published in another communication.

In the present paper, a slightly different method of determining the elastic constants of crystals is described. It has been found that under suitable conditions, even a piezo-electric plate of uniform thickness can be thrown into forced vibrations giving a continuous frequency spectrum, the spurious maxima appearing with a wedge being thus altogether absent. Using such a plate, the elastic constants of ammonium alum, barium nitrate and two varieties of beryl have been determined.

2. Experimental Technique

A Z-cut tourmaline plate is ground to uniform thickness of about 2 mm. and silvered on the two flat sides. If R.F. oscillations from a sufficiently powerful oscillator are impressed on it, it would execute what may be called "pure" piezoelectric thickness oscillations of the same frequency as the impressed R.F. oscillations, provided we are fairly remote from a resonance frequency. The amplitude would naturally be very much smaller than that which the plate would acquire while in resonance. However, with a sufficiently powerful H.F. oscillator to drive the plate, these "pure" oscillations may themselves be used for exciting in their turn the mechanical resonant frequencies of a non-piezo-electric plate. Such oscillations are then communicated to a liquid and the rest of the procedure is identical with that in the wedge method referred to in the introduction.

The oscillator used is a Hartley shunt-feed type using R.C.A. 8C7 valve. The mean thickness of the tourmaline plate used is (2·18 ± ·02) mm. The oscillations of the plate alone are studied in the first place. The mean fundamental frequency is found to be (1·82 ± ·02) Mc/sec. A resonant oscillation can be easily distinguished from the "pure" one from the nature of the diffraction pattern. At resonance, the pattern contains as many as 10 orders (using transformer oil as the liquid) at the fundamental frequency and more than 4 at the higher harmonics. On the other hand, the pattern due to the "pure" vibration contains only one bright first order, a very feeble second order appearing very rarely near the fundamental frequency range, *i.e.*, between 1·6 to 1·8 and 1·84 to 2 Mc/sec. For the rest, the plate gives only a single bright order from approximately 0·8 to 7 Mc/sec. After 7 Mc/sec, the pattern becomes rather faint but remains continuous up to 8 Mc/sec.

This plate is used to measure the elastic constants of (*a*) Ammonium alum,[3] (*b*) Barium nitrate,[3] and (*c*) two varieties of beryl* which have all been worked previously by the wedge method.

3. EXPERIMENTAL OBSERVATIONS AND RESULTS

The following observations may be mentioned. Firstly, when the piezo-plate is used to excite the natural frequencies of the crystals, no spurious maxima appeared in diffraction so that every diffraction pattern observed corresponds to a vibration mode of the crystal. Secondly, round every frequency of a mode of oscillation of the crystal, a group of frequencies, differing very minutely from each other occur. This is due to minute variations in thickness. All the frequencies observed fall, however, into definite groups, and the groups can in turn be classified into two or three types, each type containing a fundamental mode and its harmonics. Table I gives the complete data obtained with a Z-cut beryl plate and is intended to illustrate how the analysis of the data is done:

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* The wedge method values for beryl have been taken from unpublished work done by B. Ramachandra Rao, in these Laboratories.

TABLE I

Green variety beryl; Z-cut plate

Thickness = 1·495 mm.; density 2·720 gm/cm.^{3}

Frequencies		Mode	Corresponding Elastic constant
With a good tourmaline wedge	With a tourmaline plate		
1·7 .. I 1·73 .. I	..1·7 1·72 .. I	torsion (t)	C_{44}
*1·9 .. S	x 1·82 .. I	(fundamental of the piezo-plate)	—
*2·9 .. S	..		
3·1 .. V. I 3·15 .. V. I 3·18 .. I	3·12 3·15 ..V. I 3·18	longitudinal (l)	C_{33}
*3·3 .. S	..		
3·4 .. I 3·45 .. S	3·38 3·40 .. I 3·42	2 × (t)	C_{44}
*4·28 .. S	..		
5·07 .. I 5·08 .. S	5·07 5·072 .. I	3 × (t)	C_{44}
*5·28 .. S	..		
*5·4 .. W	..		
6·3 .. V. I	6·3 6·31 ..V. I	2 × (l)	C_{33}
*6·5 .. S	..		
*6·8 .. W	..		
*8·98 .. W	..		
*9·12 .. W	..		
9·48 .. I 9·49 .. I 9·50 .. I	9·47 9·48 .. S 9·49	3 × (l)	C_{33}

In the above Table, V.I. denotes very intense and more than one order; I, intense; S, strong but less than intense; W, weak; and frequencies marked with (*) are spurious wedge maxima. In the wedge method, the spurious maxima are minimized by a careful selection of the wedge; and finally scored off in analysis since their harmonics do not appear. Table I also shows that using the plate there are no spurious maxima except the one at 1·82 which is the fundamental frequency of the plate itself. Its second harmonic does not occur. After sorting out the frequencies, the mean value corresponding to each mode is found, and the effective elastic constant calculated in the usual way.

Thus, from the table, the longitudinal fundamental comes out as 3·153 Mc/sec, and the torsional one as 1·7 Mc/sec giving respectively $C_{33} = 24\cdot18$ and $C_{44} = 7\cdot03$ in units of 10^{11} dynes/cm.^{2}

A third observation of interest is that if the plate under investigation is very thick and non-uniform in structure, with cracks in the material, the intensity of the pattern obtained with a piezo-plate is considerably less than that with a wedge. In the extreme case, with a plate 2 mm. thick of a micro-crystalline aggregate like quartzite with a highly inhomogeneous structure, the response is very poor. Also the thinner plates of beryl were more easy to work with by this method than the thicker ones.

The elastic constants obtained with various crystals are given in Table II in units of 10^{11} dynes/cm^2.

TABLE II

Substance	C_{11}		C_{33}		C_{44}		C_{12}		C_{13}	
	With Wedge	With Plate	With Wedge	With Plate	With Wedge	With Plate	With Wedge	With Plate	With Wedge	With Plate
1. Ammonium Alum	2·50	2·51	..	..	0·8	0·81	1·06	1·08	..	..
2. Barium Nitrate ..	6·02	6·04	..	..	1·21	1·22	1·86	1·86	..	..
3. Beryl (spotted green variety)	27·81	28·00	24·8	24·80	6·61	6·58	10·01	9·9	6·77	6·70
4. Beryl (Sea-green variety)	29·71	28·73	26·50	24·18	7·54	7·02	10·26	9·91	7·39	7·29
Voigt's values for Beryl by static Methods	26·95		23·61		6·54		9·60		6·61	

It may be noted here that for the successful working of this method, the crystal plate under investigation should be sufficiently thin, so that absorption of the comparatively small ultrasonic energy in the medium is minimised. As has already been mentioned, plates like that of quartzite with many crevices and cavities cannot be investigated by this method without increasing the electrical load on the piezo-plate beyond safe limits.

The elastic constants obtained in the case of ammonium alum, and barium nitrate with the plate agree very well with those obtained by the wedge methods. The agreement in the case of beryl is fairly good.

Voigt's[4] values for beryl are considerably lower than those obtained in the present investigation. The values of elastic constants obtained by using static methods (Voigt) are usually lower than those obtained by dynamic methods. Moreover, beryl occurs in a large variety of slightly differing compositions giving slightly differing elastic constants.

4. SUMMARY

A modified method of finding the elastic constants of crystalline substances using a piezo-electric plate of uniform thickness is described in the present paper. The conditions under which the method can be successfully employed have been discussed. The elastic constants of ammonium, alum, barium nitrate and beryl have been determined by using this method. Results compare well with those obtained by the wedge method.

ACKNOWLEDGEMENT

The author expresses his thanks to Prof. S. Bhagavantam under whose guidance this work was done.

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ELASTIC CONSTANTS OF AMMONIUM CHLORIDE AND AMMONIUM BROMIDE

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1. Introduction

Many of the physical properties of the alkali halides, like the thermal expansion coefficients, molecular refractions, etc., have been determined by various authors and summarised by Wooster (1938). Recently, the Raman effect (R. S. Krishnan, 1947) and the Faraday effect (S. Ramaseshan, 1947) for some of the single crystals of these were studied in this laboratory, so that there is a large amount of available data concerning them. The comparatively simple structure of these crystals has also made it possible to attempt a theoretical correlation between the structure and the observed data. Among the elastic properties of these substances, the cubical compressibilities have been determined for almost all of them; but the separate elastic constants of the single crystals are determined for only a few.

It is proposed therefore to determine the separate constants of ammonium chloride and ammonium bromide. A word about the choice of these ammonium halides is not out of place. Though the cation is really complex, the hydrogen ions, imbedded in the distribution of the negative charge in a symmetrical tetrahedral arrangement do not greatly affect the structure so that they can be considered along with the other alkali halides, as is usually done. Another point of interest regarding these two halides is that they have the body centred caesium chloride structure at room temperature and change over to the rock-salt type at high temperatures.

The single crystals of ammonium chloride are of fairly good size for the method of investigation used, being about ·8 cm. × ·8 cm. × ·5 cm., without any inclusions in them. Those of NH_4Br, however, have a number of inclusions in the material so that observations on them are rather tentative and approximate.

2. Experimental Technique

The method of determining the elastic constants is to send an ultrasonic wave, using a piezo-electric plate of uniform thickness, developed in the Andhra University laboratories. The details of the experimental technique are given in another paper by one of the authors (Sundara Rao) appearing in this Symposium. The outlines of the method may be given as follows. The inverse piezo-electric effect for a piezo-plate of uniform thickness is given by the relation:

$$\delta = d_{ij} \cdot U \tag{1}$$

for the thickness displacement of the plate, where δ is the amount of contraction or expansion; U, the difference of potential applied to the faces normal to the thickness direction, and d_{ij} the appropriate piezo-electric modulus for that direction. If therefore U is of the form:

$$U = U_0 \cos \nu t, \tag{2}$$

the plate executes forced vibrations with approximately the same frequency as ν. Therefore, if an oscillator of a sufficiently good R.F. voltage and power output of variable frequency is used as a driver for the piezo-plate, we have at once a source of continuous frequency ultrasonic energy. The latter output, however small, was found to be sufficient to work with, when a non-piezo-plate, under investigation, of uniform thickness, is acoustically coupled to the piezo-plate. This is effected by forming a condenser with two parallel metallic plates, between which is placed the combination of the piezo- and the non-piezo-plates placed with their thicknesses parallel, and with a drop of transformer oil in between them to accomplish the acoustic contact. This condenser is now connected in parallel with the variable condenser of the oscillator. At the natural mechanical frequency (or a harmonic) of the crystal plate, it acts as a resonator to the driving piezo-electric oscillations of the small amplitude, given by (1) and (2) above, when the frequency of the oscillator coincides with that of the former. In other words, it is the resonator principle that makes it possible to utilize the forced oscillations of the piezo-plate to throw the crystal plate into ultrasonic vibrations at the latter's natural frequency. These ultrasonic vibrations are communicated to a transparent liquid, touching the underneath of the non-piezo-plate. The detection of the ultrasonic waves in the liquid is effected by using Debye Sears' phenomenon.

As regards the necessary crystal sections, since the crystals belong to the cubic symmetry, a plate cut normal to the cube edge, (100) section and another cut parallel to one of the edges and making equal intercepts on the other two axes, (110) section, are enough to determine C_{11}, C_{12}, and C_{44}, which are the three non-vanishing elastic constants required to describe the elastic behaviour of a cubic crystal under stress. Specifically, the sections and the effective elastic constants associated with them are given in Table I below.

TABLE I

Section	Effective Elastic Constants
(100)	C_{11} ; C_{44}
(110)	$\frac{1}{2}(C_{11}+C_{12}+2C_{44})$; C_{44}; $\frac{1}{2}(C_{11}-C_{12})$
(111)	$\frac{1}{3}(C_{11}+2C_{12}+4C_{44})$; $\frac{1}{3}(C_{11}-C_{12}+C_{44})$

The third section (111), if available, can be used to check the results obtained from the other two. The effective elastic constants can be computed from the relation:

$$f_r = \frac{1}{2d}\left(\frac{C_E}{\rho}\right)^{\frac{1}{2}}, \tag{3}$$

where f_r is the fundamental resonance frequency, d, the thickness of the plate, C_E, the effective elastic constant, and ρ the density of the plate.

A push-pull Hartley oscillator of variable frequency for R.F. power generation, and plates of about 1 mm. to 1·5 mm. thickness are used.

3. EXPERIMENTAL RESULTS

As mentioned in the introduction, the crystals of NH_4Br are not very good, so that the diffraction patterns were not as sharp as in the case of NH_4Cl. However, a sort of average frequency is made out of repeated observations, and by selecting the most intense of the patterns as corresponding to the resonance frequency. In any case, the deviation as calculated from the entire frequency data would not be more than 8 to 10 per cent. and in all probability, the tabulated values are lower than the possible actual ones by so much. With this degree of uncertainty about the values for NH_4Br, the following Table II gives the values obtained in the case of the two halides. In the last two columns, the calculated and the observed (Bleick, 1934) values of the bulk modulus are given, the former having been obtained from

$$K = \tfrac{1}{3}(C_{11} + 2C_{12}) \tag{4}$$

All the values are given in units of 10^{11} dynes cm.$^{-2}$

TABLE II

No.	Substance	C_{11}	C_{12}	C_{44}	K (calculated)	K (observed)
1	NH_4Cl	3·90	0·72	0·68	1·77	1·736
2	NH_4Br	2·96	0·59	0·53	1·38	1·680

4. DISCUSSION OF THE RESULTS

Though it is not possible to draw many quantitative conclusions from the above data, firstly because data concerning no other crystals having the CsCl structure type are available in the literature, and secondly because of the uncertainty of the values of NH_4Br, we can see, that they exhibit the same sort of gradation in the values as do the other alkali halides. Another point of interest comes out if we compare the values with the lattice spacings. Thus for NH_4Cl, the interionic distance *i.e.*, the distance between one ion and the nearest neighbour of opposite sign is 3·34 and that for NH_4Br, 3·51 (Slater, 1939) in angstroms. A comparison of these values with the elastic constants shows that as the interionic distance increases, the elastic resistance of the crystals decreases (ionic charge remaining the same). In other words, the closer the packing of the ions in the crystal, which means a lesser interionic distance, the larger are the elastic constants. An examination of the elastic constants of the other alkali halides, for which values are available in the literature (R.F.S. Hearmon, 1946) and tabulated below, also shows the same variation.

TABLE III

Substance	r_0 in Angstroms	C_{11}	C_{12}	C_{44}
LiF ..	2·01	9·81	3·61	6·28
Nacl ..	2·81	6·23	1·37	1·28
NaBr ..	2·98	3·26	1·31	1·33
KCl ..	3·14	3·72	0·81	0·79
KBr ..	3·29	3·33	0·58	0·62
KI ..	3·63	2·67	0·43	0·42

The substances in Table III, all belong to the rock-salt structure, but the regular decrease of the elastic constants with the increasing interionic distance r_0 (Slater, 1939) is quite obvious. In fact, from the above table, we see after a little calculation, that for most of the crystals (LiF being an outstanding exception) the relation

$$C_{ij} \simeq a_{(ij)}\, r_0^{-4} \tag{5}$$

holds good, where C_{ij} represents C_{11}, C_{12} or C_{44}, and a_{ij} is a typical constant for each (ij), for a particular structure type. In other words, the relation (5) gives

$$\frac{C_{ij}^{ah}}{C_{ij}^{a'h'}} \simeq \left(\frac{r_0^{ah}}{r_0^{a'h'}}\right)^{-4} \tag{6}$$

where C_{ij}^{ah} stands for the elastic constant C_{ij} of the alkali halide with cation '*a*' and anion '*h*' and similarly for c_{ij}^{ah}. Thus if we take NaCl and KCl, we have, for instance,

$$\frac{C_{12}^{\mathrm{NaCl}}}{C_{12}^{\mathrm{KCl}}} = \frac{1\cdot 37}{\cdot 81} = \left(\frac{2\cdot 81}{3\cdot 14}\right)^{-4\cdot 094} \simeq \left(\frac{r_0^{\mathrm{NaCl}}}{r_0^{\mathrm{KCl}}}\right)^{-4}$$

and so on.

A similar calculation for NH_4Cl and NH_4Br, belonging to CsCl structure type can be made, and we have:

$$\frac{C_{11}}{C_{11}'} = \frac{3\cdot 9}{2\cdot 96} = \left(\frac{3\cdot 34}{3\cdot 51}\right)^{-5\cdot 302}$$

$$\frac{C_{12}}{C_{12}'} = \frac{\cdot 72}{\cdot 59} = \left(\frac{3\cdot 34}{3\cdot 51}\right)^{-3\cdot 864}$$

$$\frac{C_{44}}{C_{44}'} = \frac{\cdot 68}{\cdot 53} = \left(\frac{3\cdot 34}{3\cdot 51}\right)^{-4\cdot 787}$$

where the undashed constants belong to NH_4Cl and dashed ones to NH_4Br. Except in the case of C_{12}'s, we see that the value of the index is about − 5; but this is inconclusive because of the probably low values of NH_4Br. Accurate determination of the elastic constants with better specimens of NH_4Br crystals might yield better results for '*n*' the index.

Another point of interest in the above results is that Cauchy's relations are nearly satisfied for these crystals, as in the case of the other alkali halides. For cubic crystals, Cauchy's relations give $C_{12} = C_{44}$. Table II shows that it is approximately so. It is in a sort of agreement with the theoretical requirements (Born, 1932) of a crystal in which all the atoms or (ions) are at the centres of symmetry.

In conclusion, the authors wish to thank Prof. R. S. Krishnan for his kind encouragement and guidance.

5. SUMMARY

The elastic constants of NH_4Cl and NH_4Br single crystals are determined by using the ultrasonic piezo-plate method. The relation between the elastic constants and the interionic distances for the alkali halides and the ammonium halides in question has been discussed. Cauchy relation has been verified in the case of NH_4Cl and NH_4Br.

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RAMAN SPECTRA OF SODIUM AND POTASSIUM TARTRATES

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1. Introduction

Studies on the Raman spectra of crystalline tartrates are of great theoretical interest as they may be expected to throw some light on the peculiar electric properties of such crystals. Special mention may be made of crystals like potassium tartrate ($K_2C_4H_4O_6$, $\frac{1}{2}$ H_2O) and ethylene diamine tartrate ($C_6H_{14}N_2O_6$) which are finding increasing application as piezo-electric oscillators. In view of the fact that large clear crystals of tartrates can be easily grown from solutions, it is surprising to note that very little systematic work has been done on their Raman spectra. The author has therefore undertaken a systematic investigation of the Raman spectra of crystalline tartrates and the present paper describes the results obtained with sodium and potassium tartrates.

Working with a single crystal, Gupta (1938) was the first to record the spectrum of sodium tartrate which exhibited five lines with frequency shifts 889, 990, 1071, 1118 and 1215 cm.$^{-1}$ The Raman spectrum of potassium tartrate has been investigated by Canals and Peyrot (1938) using the powder technique and by Laksmana Rao (1941) using a single crystal. While the former authors recorded nine frequency shifts all lying above 1200 cm.$^{-1}$, Rao reported no less than 17 lines including 3 low frequency lines and 1 water band. In view of the complicated nature of both sodium and potassium tartrate crystals, the results obtained by earlier authors are evidently incomplete. This may be attributed to the fact that they used the λ 4047 and λ 4358 radiations of the mercury arc for excitation.

2. Experimental Details

Single crystals of sodium and potassium tartrates were grown by the method of slow evaporation from aqueous solutions of the pure salts. Great care had to be taken in adjusting the saturation of the solution and maintaining constancy of the temperature of the room. The largest crystal grown had the following dimensions: 3 × 2 × 1 cm. In the case of sodium tartrate the longer side of the crystal was parallel to the (100) face. The (010) face was not well developed. In the case of potassium tartrate also, the length of the crystal was along the (100) face.

As the tartrates are transparent to the ultra-violet, the 2536 Hg resonance radiation was used for exciting the Raman spectrum from a specially designed quartz arc. As will be evident from the later sections, this has helped to get a wealth of data regarding the Raman spectrum especially in the region of low frequency shifts.

The crystal under investigation was held facing the most intense portion of the arc, near the front wall of the quartz tube towards which the discharge was deflected. The light scattered from the crystal was condensed on the slit of a Hilger E3 Quartz Spectrograph. In the case of sodium tartrate, light was incident along the '*a*' axis, and the scattered light was taken along the *c*-axis. In the case of potassium tartrate, light was incident along the '*a*' axis and the scattered light was taken along the direction perpendicular to this axis. The 2536 radiation in the scattered light was suppressed before its entry into the spectrograph by absorption. With a slit width of 0·035 mm. and using special rapid plates, exposures of the order of 48 hours were given to get intense photographs of the Raman spectra of both the tartrates. During such long exposures a disturbing effect was noticed, namely that the portion of the crystal facing the arc became frosted due to heating, in spite of efficient cooling by a fan. Therefore, fresh crystals had to be used every five hours. In replacing the crystals care was taken to see that the same orientation was adopted. The plates were measured under a Hilger cross-slide micrometer.

3. RESULTS

Photographs of the Raman spectra of sodium and potassium tartrates are reproduced in Fig. 1 (*a*), (*c*), together with a spectrum of the mercury arc for purposes of comparison, Fig. 1 (*b*). The corresponding microphotometric records are shown in Fig. 2. The positions of the lines are marked for clarity. The frequency shifts are listed below in Table I. The figures given in brackets represent visual estimates of the relative intensities of the lines. Laksmana Rao's values for the frequency shifts in the case of potassium tartrate are shown in column 3. The author's results are in close agreement with those of Laksmana Rao.

TABLE I

Sodium tartrate (Frequency shifts in cm.$^{-1}$) Author		Potassium tartrate (Frequency shifts in cm.$^{-1}$) Author		Potassium tartrate (Laksmana Rao)
42	(5)	33	(15)	
83	(5)	78	(8)	77
110	(4)	106	(15)	103
134	(8)	153	(5)	150
188	(8)	172	(15)	
205	(3)			
231	(3)	235	(2)	
248	(5)			
279	(4)	281	(4)	
302	(3)	309	(3)	
		339	(4)	
353	(3)			
		379	(4)	
488	(4)	493	(6)	493
532	(8)	528	(8)	531
		603	(2)	603
697	(4)	697	(3)	
813	(15)	809	(10)	807
849	(5)	850	(6)	846
893	(8)	897	(6)	889
917	(4)	919	(8)	
		955	(5)	
990	(2)	992	(2)	995
1037	(3)			
1072	(8)	1072	(2)	1073
1112	(15)	1110	(8)	1110
1209	(8)	1218	(10)	1219
1247	(3)	1244	(8)	
1287	(3)	1281	(2)	
		1315	(3)	
		1322	(2)	1323
1352	(5)			1351
1381	(3)	1397	(4)	
1404	(4)	1418	(15)	
1432	(6)	1429	(20)	1425
1463	(8)			
1496	(2)			
1560	(3)	1560	(5)	
1585	(6)	1585	(5)	
1604	(3)	1602	(2)	
		1628	(2)	
		1659	(3)	
2935	(20)	2926	(20)	2926
2981	(20)			
3285		3283		
3399		3336		3336
3471		3435		
3514				

The displaced lines are clearly seen on the microphotometric record. Most of them can be identified on the reproduced photographs. The recorded spectra show 40 frequency shifts in the case of sodium tartrate, and 39 in the case of potassium tartrate. Of these, 31 lines and 4 water

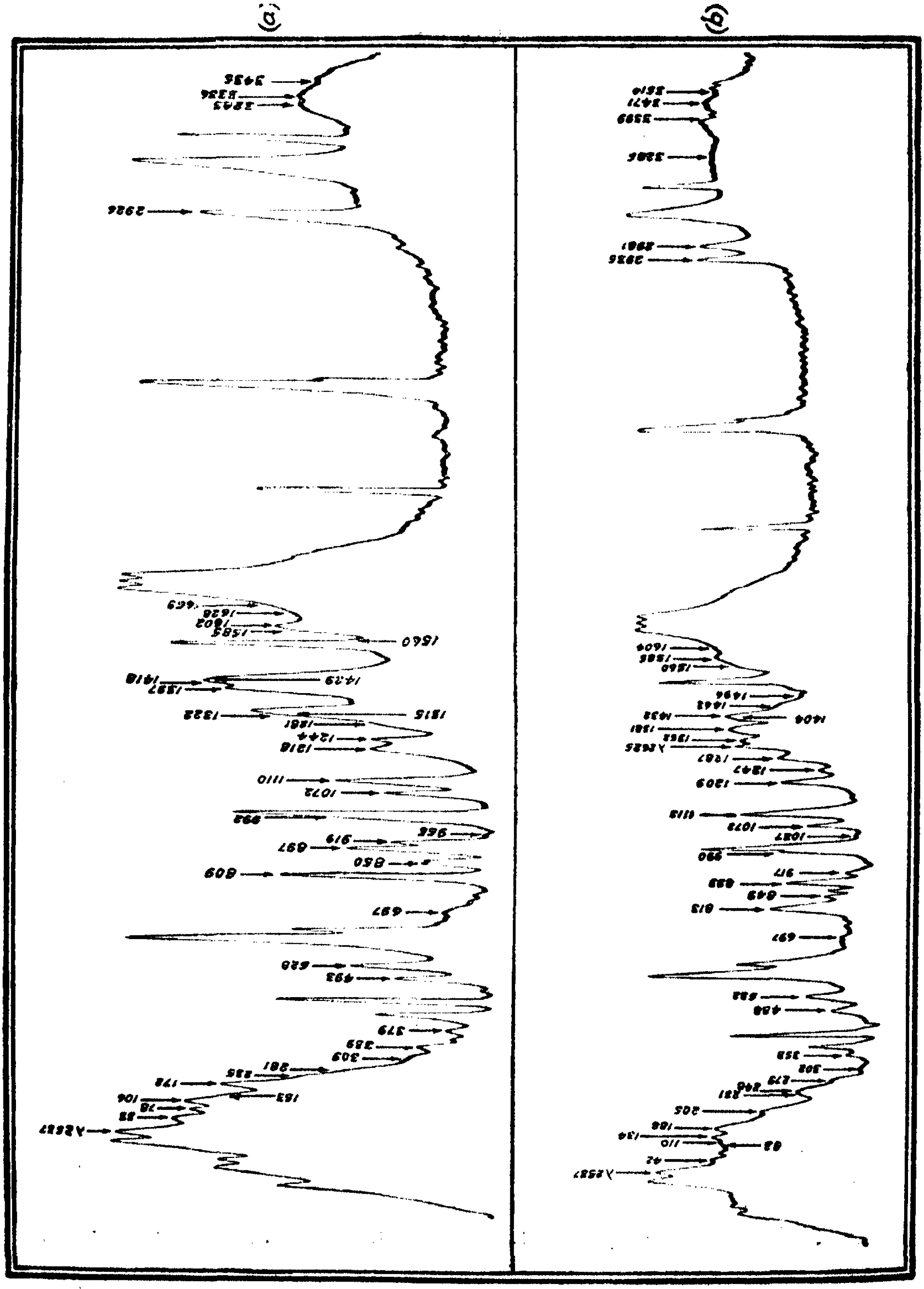


FIG. 2

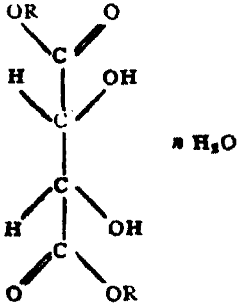
Micro-photometric record— (*a*) Potassium Tartrate (*b*) Sodium Tartrate.

bands in sodium tartrate and 19 lines and 2 water bands in potassium tartrate have been recorded for the first time. As is to be expected, there is a close correspondence between the Raman spectrum of sodium tartrate and that of potassium tartrate in the region of frequency shifts 230 to 3500 cm.$^{-1}$ The Raman lines falling in this region are evidently due to the internal oscillations of the tartrate ion and that of the water molecule. The existence of a line at 603 cm.$^{-1}$ reported by Laksmana Rao could not be identified in the spectra taken by the author since it coincides with the mercury line λ 2576. Besides the Raman lines given in Table I, a weak band in the neighbourhood 1400 cm.$^{-1}$ appears to be present in the case of sodium tartrate, though it is not present in the case of potassium tartrate. Of the three water bands observed with potassium tartrate, the band at 3283 cm.$^{-1}$ is the weakest. In the case of sodium tartrate, on the other hand, the band at 3399 cm.$^{-1}$ is the most intense, and the one at 3285 is the least intense. The bands at 3471 and 3514 are less broad than the other two.

The low frequency lines can be clearly seen in the spectra of both the crystals, though they are more intense in the case of potassium tartrate. The two lattice lines at 33 and 172 cm.$^{-1}$ of potassium tartrate, and all the six lattice lines of sodium tartrate have been recorded for the first time. The lines 134 and 188 cm.$^{-1}$ in sodium tartrate are more intense than the other lattice lines. The line 188 cm.$^{-1}$ is rather broad. This may be attributed to the superposition of the weak low frequency water band at 170 cm.$^{-1}$ The lines 33, 106 and 172 cm.$^{-1}$ observed in the spectrum of the potassium tartrate are more intense and broader than the lines 78 and 153 cm.$^{-1}$

4. DISCUSSION

Sodium tartrate belongs to the orthorhombic class and has two molecules of water of crystallisation. Potassium tartrate belongs to the monoclinic system, and has one molecule of water of crystallisation for two molecules of potassium tartrate. Their chemical constitutional formula is given as



where R represents the metallic ion and *n* the number of water molecules.

The structures of both sodium and potassium tartrates have not been fully worked out by X-ray analysis.

The observed Raman lines can be roughly classified into three groups—lattice lines, frequencies due to the tartrate ion and water bands.

Lattice Oscillations.—Table II shows lattice frequencies observed in the spectra of sodium tartrate, potassium tartrate, Rochelle salt and tartaric acid.

TABLE II

Sodium tartrate (Author)	Potassium tartrate (Author)	Rochelle Salt (Nedungadi) (1940)	Tartaric acid (Gupta)
42	33	39	36
83	76	88	80
110	106		103
134	153	132	124
188	172		
205			

As can be seen from the above table, the lattice frequencies in the case of potassium tartrate have lower values as compared with the corresponding frequencies in the case of sodium tartrate and Rochelle salt. The lowering of frequency in the case of potassium tartrate may be attributed to the heavier mass of the potassium ion than sodium or sodium and potassium combined. A more complete study of the spectra of Rochelle salt and tartaric acid using the ultra-violet technique is necessary before one can attempt to give a proper interpretation of the observed lattice lines in sodium and potassium tartrates.

Frequencies due to the tartrate ion.—Table III gives the frequency shifts of the Raman lines due to the internal oscillations of the tartrate ion as observed in the spectra of crystalline sodium and potassium tartrates (author), Rochelle salt (Nedungadi) and of sodium tartrate solution (Edsall) (1937).

The most intense line at 2926 cm.$^{-1}$ observed in potassium tartrate and the lines at 2935 and 2981 cm.$^{-1}$ in sodium tartrate are obviously due to C–H oscillation. The interesting fact is that whereas only one line is observed in the case of potassium tartrate, two lines appear in sodium tartrate. Sodium tartrate belongs to the orthorhombic class, whereas potassium tartrate belongs to the monoclinic system. The appearance of two lines in the case of sodium tartrate cannot be attributed to any splitting

TABLE III

Sodium tartrate	Potassium tartrate	Rochelle salt	Sodium tartrate solution
231	235		239
248		249	
279	281		
302	307		
	339		
353			
	379		378
488	493	485	491
532	528	532	532
	603	611	618
		641	
697	697	691	
813	809	811	805
849	850		
893	897	891	893
	919	915	
917	955		
990	992	990	992
1037			
1072	1072	1070	1068
1112	1110	1112	1121
1209	1218	1210	1224
1247	1244		
1287	1281	1292	
	1315		1310
	1322		
1352		1347	
1381		1379	1370
	1397		
1404	1418		1418
1432			
1463	1429	1425	
1496			
1560	1560		
1585	1585		
1604	1602		1617
	1628		
	1659		
2935	2926	2935	2936
2981		2979	

of the oscillations due to lower symmetry, because sodium tartrate is more symmetric than potassium tartrate. The group of lines in the neighbourhood of 900 cm.$^{-1}$ (lines 813, 849, 893, 917, 990 in sodium tartrate, and lines 809, 850, 897, 919, 955 and 992 in potassium tartrate) is obviously due to linear *C–C* oscillations of the ion. The three lines at 239, 491 and 532 cm.$^{-1}$, observed in the spectrum of the solution, have been attributed to the deformation oscillations of the carbon chain. The appearance of these three lines in the spectra of crystalline sodium tartrate, potassium tartrate and Rochelle salt without appreciable change in frequency shifts indicates that ionisation has no effect on these frequencies. The three lines appearing in the region 275–350 cm.$^{-1}$ in the spectra of both sodium and potassium tartrates may also be attributed to deformation oscillation of the carbon chain arising from its increased complexity. The group of lines falling in the region 1035–1380 cm.$^{-1}$ may be attributed to the oscillations of the $-\overset{|}{\underset{|}{C}}-OH$ group. The carbonyl frequency ~ 1700 cm.$^{-1}$ observed in other organic acids and compounds does not appear in the spectra of tartrates. Hibben (1939) attributed the line 1617 cm.$^{-1}$ observed in the spectrum of tartaric acid, to the ionised carboxyl group. So the group of lines appearing in the region 1560–1604 cm.$^{-1}$ in the spectra of both the salts can likewise be attributed to oscillations of the ionised carboxyl group. The lines 1432 and 1463 of sodium tartrate, and 1429 of potassium tartrate may be attributed to C–H bond-bending oscillations.

The ionised carboxyl group resembles a bent triatomic molecule $\left[R-C\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}\right]^-$. The calculated frequency of the symmetric valence oscillation of this group falls at 1400. The line 1381 in the case of sodium tartrate and the one 1397 in the case of potassium tartrate correspond to this oscillation. The lines 1404 and 1418 can then be attributed to asymmetric valence oscillation of this group. A symmetric deformation oscillation at 600 must also be present. This could not be detected in the spectra taken with λ 2537 excitation as it would fall on the intense mercury line λ 2576.

The spectrum of potassium tartrate exhibits two faint lines at 1659 and 1628 cm.$^{-1}$ which may be assigned as the combination of the intense lines 809 and 850, and the overtone of the line 809.

The four water bands observed in the case of sodium tartrate have nearly the same frequency shifts as the four water bands of Rochelle salt (3262, 3400, 3468 and 3534) recorded by Nedungadi. It is of some interest to point out that the band with the lowest frequency shift corresponds with the band 3200 cm.$^{-1}$ observed in the case of pure water.

In conclusion, the author wishes to express his grateful thanks to Prof. R. S. Krishnan for his guidance and encouragement.

5. SUMMARY

Using λ 2536 for excitation, the Raman effect of single crystals of sodium and potassium tartrates has been investigated. The recorded spectra exhibit forty Raman lines in the case of both sodium and potassium tartrates.

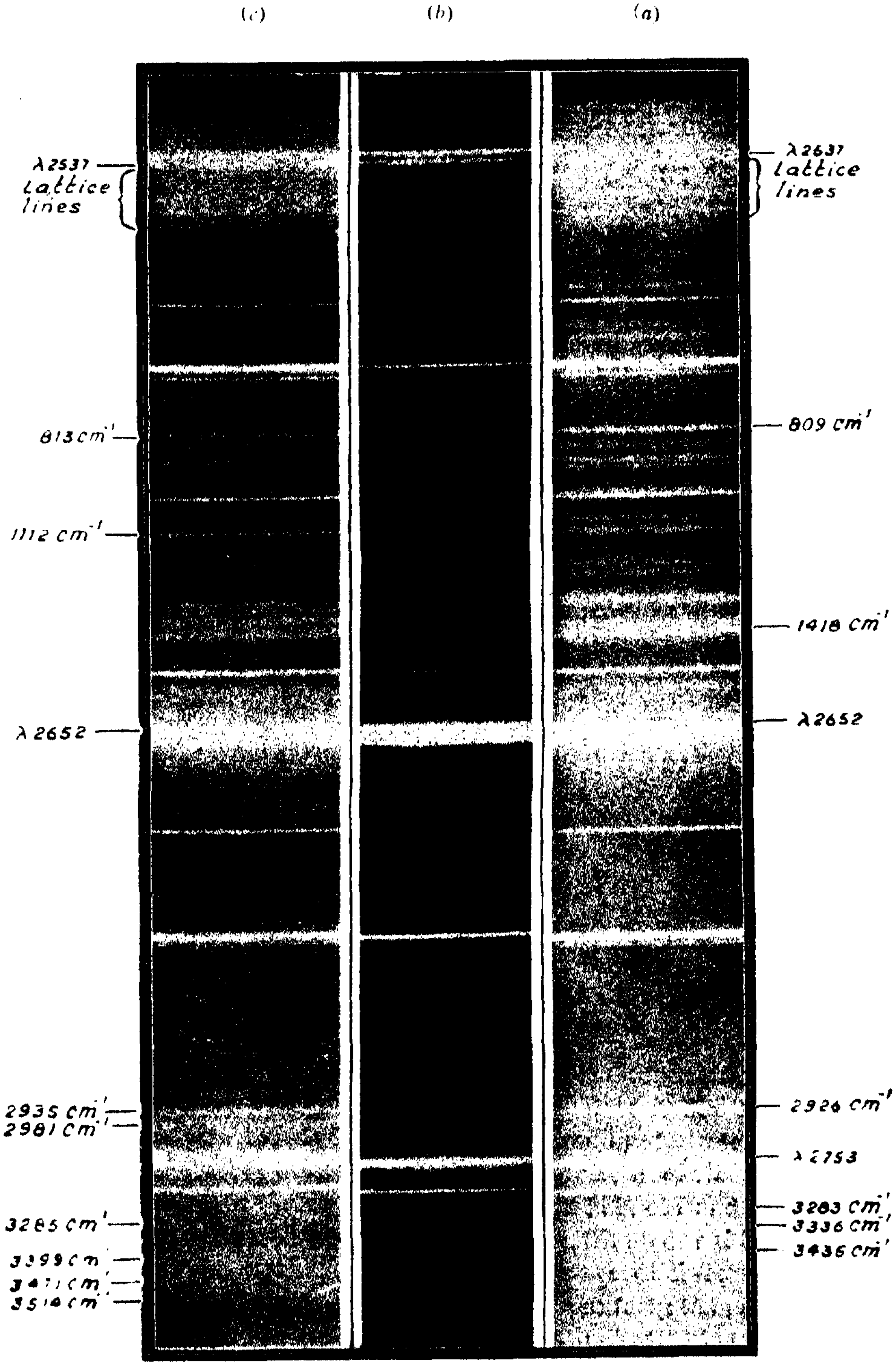


FIG. 1. (*a*) Raman spectrum of potassium tartrate
(*b*) Comparison spectrum of mercury arc
(*c*) Raman spectrum of sodium tartrate

As many as thirty-four lines in the case of sodium tartrate, and twenty-two in the case of potassium tartrate, have been recorded for the first time. The observed frequencies can be classified under three heads—namely, lattice spectrum, internal frequencies due to tartrate ion, and water bands. A tentative assignment has been given to important groups of lines appearing in the spectrum.

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RAMAN SPECTRUM OF ETHYLENE DIAMINE TARTRATE

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1. INTRODUCTION

IT is known that ethylene diamine tartrate ($C_6H_{14}N_2O_6$) has elastic modes of vibration with zero temperature coefficient of frequency and high electromechanical coupling constants. Because of these special properties, this crystal is finding increasing application as filters in oscillators in place of quartz which is difficult to obtain in large sizes. A detailed study of its Raman spectrum may be expected to throw some light on the mechanism of its peculiar electric behaviour. Besides, it will also give some information regarding the existence or otherwise of "free rotation" about the C–C bond. Surprisingly enough, so far no one has studied the Raman spectrum of ethylene diamine tartrate. A detailed investigation on the Raman spectrum of ethylene diamine tartrate and also the effect of crystal orientation on its spectrum has therefore been undertaken by the present author and the results are given in this paper.

2. EXPERIMENTAL

The specimen of ethylene diamine tartrate used in the present investigation had well developed faces with the following dimensions—9 × 6 × 4 cm. This crystal was grown in the Bell Telephone Laboratories, Murray Hills, New Jersey, U.S.A., and was presented to Prof. Sir C. V. Raman, who very kindly placed the same at the disposal of the author. Though the major portion of the crystal was clear, imperfections existed in certain places, probably due to the conditions and the mode of growth of the specimen. As the crystal got coloured intensely yellow on exposure to ultra-violet light and became opaque to λ 2536 radiation, λ 4358 and λ 4047 excitation had to be used for recording the Raman spectrum. Light from a quartz mercury arc was focussed on the crystal by a glass condenser. The scattered light was condensed on the slit of a two-prism glass spectrograph. A trial exposure taken with the 4047 and 4358 excitation exhibited a continuum due to fluorescence extending over λ 4500–5000. This was found to overpower the Raman lines and thus prevented the latter from being recorded properly. The use of a filter, made up of a weak solution of iodine in carbon tetrachloride in the path of the incident light reduced the intensity of the continuous spectrum to some extent. Using a slit width of 0·075 mm. and Ilford Selochrome plates, exposures of the order of 36 hours were found to be sufficient to get pictures with reasonable intensity.

Six different spectrograms can be got by varying the orientation of the crystal relatively to the directions of incidence and scattered beams. Only three spectrograms were taken in the present case, with the following orientations:—(1) incident light being perpendicular to 100 face, and scattered light being perpendicular to 001 face, (2) incident light being perpendicular to 100 face, and scattered light being perpendicular to $\bar{1}\bar{1}0$ face, and lastly incident light being perpendicular to 001 face and scattered light being perpendicular to $\bar{1}\bar{1}0$ face. The plates were measured by direct comparison with a standard iron arc spectrum, on a Hilger cross-slide micrometer.

3. RESULTS

Three spectrograms obtained by the use of unpolarised light for different orientations of the crystal are reproduced as Fig. 1 *a*, *b* and *c*, in Plate XI. Fig. 1 *c* is particularly clear and more intense than the other two. As there was a continuum near λ 4358, Raman lines arising from the excitations of λ 4047 alone are marked on the Plate. The frequency shifts and the visual estimate of the intensities of the lines in the three orientations are given in Table I.

On the whole, thirty-five distinct frequency shifts have been recorded in the present investigation. It must be mentioned that a correct assignment of these lines in the spectrum is difficult as some of the C–H valence oscillations excited by λ 4046 are superposed over other lines excited by λ 4358. Further, lines due to N–H oscillation also fall in the same region.

An interesting observation made in the present investigation is that the Raman lines undergo marked changes in intensity for different orientations of the crystal even when the incident light is unpolarised. The lines 3010, 2985, 2946, 1459, 1432, 1110, 1060, 992, 920, 144 and 85 undergo marked changes in intensity, whereas the lines 1677, 1380, 1203, 798, 758, 723 and 102 do not show fluctuations in intensity with the three orientations of the crystal. The rest of the lines show correspondingly only slight changes in intensity. The very low frequency lines also show this behaviour.

TABLE I

Line	Intensities of the lines		
	I. L.—I00 S. L.—$\overline{11}0$	I. L.—100 S. L.—001	I. L.—001 S. L.—$\overline{11}0$
45	5	1	3
85	9	2	6
102	3	2	3
144	5	3	10
232	3	1	5
328	5	2	8
394	1	..	3
428	1	..	3
477	6	..	2
520	2	6	3
562	2	2	8
610	2	..	3*b*
642	5	..	4
723	3	5	5
758	2	3	2
798	5	5	6
897	8	3	10
920	6	2	6
992	2	1	10
1060	5	5	10
1110	4	1	2
1162	2	2	4
1203	2	3	3
1328	3	3	6
1352	3	8	5*b*
1380	2	3	3
1432	5	3	10
1459	6	2	8
1523	2	4	2
1570	1	1	3
1640	3	8	5
1677	2	4	3
2946	6	8	10
2985	10	8	20
3010	4	4	8

I. L. — incident light perpendicular to } *b* = broad
S. L. — Scattered ,, ,, ,,

4. DISCUSSION

The frequency shifts observed in ethylene diamine tartrate are listed in Table II, along with the shifts in crystalline sodium tartrate (Padmanabhan, 1948) and in liquid ethylene diamine (Ananthakrishnan, 1937).

TABLE II

Ethylene diamine tartrate	Sodium tartrate (Crystal)	Ethylene diamine (liquid)
45	42	
85	83	
102	110	
144	134	
	188	186
	205	
232	231	
	248	
	279	
328	302	333
394	353	
428		
477	488	467
520	532	510
562		
610		
642		
	697	
723		
758		
798		
	813	
	849	837
897	893	
920	917	
992	990	987
	1037	
1060	1072	1051
1110	1112	1093
1162		
1203	1209	
	1247	1240
	1287	1296
1328		
1352	1352	1360
1380	1381	
1432	1432	
1459	1463	1445
	1496	
1523		
	1560	
1570		
	1585	
	1604	
1640		
1677		
		2661
		2743
		2848
		2898
2946	2935	2932
2985	2981	
3010		
	3285	3299
	3399 Water	3366
	3471 bands	
	3514	

A perusal of the figures given in Table II reveals the following special features. Most of the Raman lines observed in the spectrum of sodium tartrate appear with very nearly the same frequency shifts in the specimen of ethylene diamine tartrate. This is particularly true of the lines 2985, 2946, 1459, 1432, 1380, 1352, 1110, 992, 920, 897 and 232 of ethylene diamine tartrate, suggesting thereby that they are due to the internal oscillations of the tartrate ion. In contrast to this, many of the Raman lines with frequency shifts higher than 2660 appearing in the spectra of ethylene diamine are not recorded in the case of ethylene diamine tartrate. Similar observations have been reported by Ananthakrishnan (1936, 1937) in the case of hydroxylamine compounds, who attributed the absence of N-H oscillations (above 3100 cm.$^{-1}$) to the ionic nature of the crystal. If the explanation is correct, the binding between ethylene diamine and tartaric acid in the ethylene diamine tartrate crystal is ionic in nature.

The low frequency lines (45, 85, 102 and 144) observed near the unmodified line, are due to lattice oscillations. Out of these four, 144 may be due to the mutual oscillations of the two groups of ethylene diamine ($C_2H_4N_2H_4$) and tartaric acid ($C_4H_6O_6$) against each other, and 85 may be due to rotation. In order to give proper assignment for the remaining ones, it is necessary to know the crystal structure of ethylene diamine tartrate.

Effect of crystal orientation.—The changes in the intensity of many of the Raman lines with orientation of the crystal have already been mentioned. This kind of behaviour of the Raman lines is to be expected in the case of monoclinic crystals. Saxena (1940) has indicated that the Raman lines observed with a crystal may be regarded as due to deformation of the optical polarisability ellipsoid of the solid produced by internal vibrations and they can be expressed in terms of the six components of the change of polarisability tensor. The selection rules for these vibrations give the particular tensor components that are responsible for them, and on these depend the intensities of the corresponding lines. From considerations of symmetry, all the vibrations in a monoclinic crystal can be classified as either symmetric or antisymmetric. The intensities of the lines due to symmetric oscillations should undergo marked changes with orientation of the crystal, whereas the lines due to antisymmetric oscillations do not undergo changes in intensity. Accordingly, the lines mentioned above which change in intensity markedly, can be treated as due to symmetric oscillations, while those which do not show changes in intensity may be classed as antisymmetric oscillations.

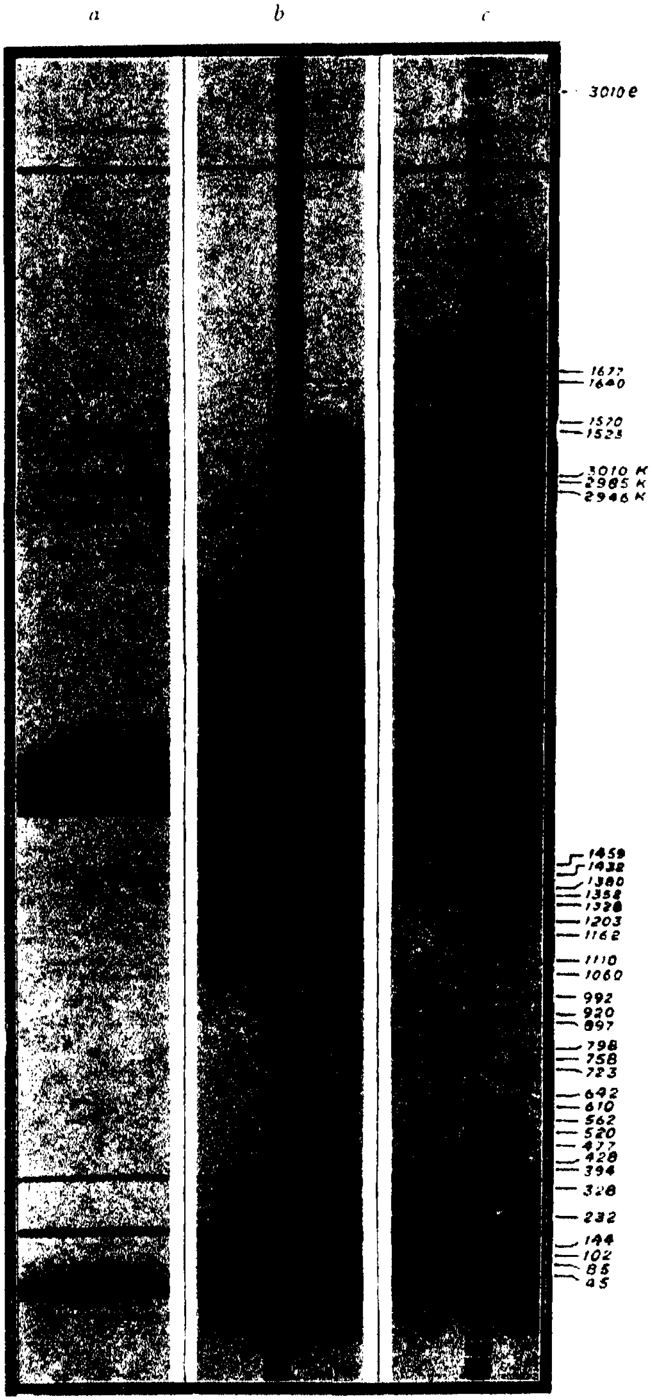
a
b
c
3010 e
1677
1640
1570
1525
3010 K
2985 K
2946 K
1459
1432
1380
1358
1328
1203
1162
1110
1060
992
920
897
798
758
723
642
610
562
520
477
428
394
328
232
144
102
85
45

Fig. 1

In conclusion, the author wishes to record his grateful thanks to Prof. R. S. Krishnan for his keen interest and encouragement during the course of this work.

5. SUMMARY

The Raman spectrum of ethylene diamine tartrate, in the form of a single crystal has been recorded for the first time. Thirty-five distinct Raman shifts are observed. Many of them have been identified as due to tartrate frequencies by comparison with the spectrum of sodium tartrate. A study of the effect of orientation of the crystal relative to the directions of incidence and observation is also made. Many of the Raman lines show marked changes in intensity by varying the orientation of the crystal. In accordance with Saxena's analysis, those lines which show change in intensity are classified as symmetrical oscillations, while those which do not show any change in intensity are regarded as due to antisymmetric oscillations.

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Saxena, B. D.	.. *Ibid.*, 1940, **11**, 209.

DESCRIPTION OF PLATE

FIG. 1. Raman spectrum of ethylene diamine tartrate.

a. Incident light perpendicular to 100 face, scattered light perpendicular to $\bar{1}\bar{1}0$ face.

b. „ „ 100 „ „ „ 001 „

c. „ „ 001 „ „ „ $\bar{1}\bar{1}0$ „

e — excitation due to λ 4358.

k — „ „ λ 4047.

RAMAN SPECTRUM OF SODIUM CHLORATE

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Received November 22, 1948
(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. INTRODUCTION

THE studies on the Raman effect in sodium chlorate are not very numerous. Among the earlier workers, Dickenson and Dillon (1929), S. T. Shen, Y. T. Yao and T. Y. Wu (1937), Venkateswaran (1938) and Kujumzelis (1938) recorded the spectrum of the aqueous solutions of sodium chlorate which exhibited four lines with frequency shifts, 930, 615, 975 and 479 cm.$^{-1}$ Daure (1929), Krishnamurthy (1930) and Venkateswaran (1938) worked on crystal powders. Among them, Daure recorded the maximum number of lines, namely eight including two low frequency lines. Recently, a more detailed investigation has been made of the Raman spectrum of sodium chlorate in the form of single crystals by Rousset, Laval and Lochet (1943). They have recorded thirteen Raman lines due to the internal frequencies of the chlorate ion and three low frequency lines. They have also measured the depolarisation factors for the intense Raman lines. From a perusal of the results obtained by the earlier workers, it is evident that very little information is available regarding the lattice spectrum of sodium chlorate, although the spectrum of the chlorate ion appears to have been very thoroughly studied. This may be attributed to the fact that the earlier workers have invariably used λ 4358 and λ 4046 radiations of the mercury arc for excitation. It was therefore felt desirable to undertake a detailed study of the Raman spectrum of sodium chlorate crystal using λ 2537 as exciter, which is specially suited for recording the lattice spectrum. The results are presented in this paper.

2. EXPERIMENTAL DETAILS

Crystals of sodium chlorate were prepared by the method of slow evaporation from aqueous solutions of the salt. The crystallisation was carried out in a chamber, the temperature of which was kept constant at about 27° C. A little quantity of urea was added to the solution to facilitate the growth of crystals of large size. The crystals were in the form of rectangular plates. The average dimensions of the crystals grown here for the present purpose were 1 × 1 × 0·5 cm.

The specimen to be investigated was mounted with its broad face vertical and facing the most intense portion of a water-cooled, magnet-controlled quartz arc which emitted the λ 2537 radiation with exceptional intensity. The light scattered transversely and emerging out through the edge of the crystal was focussed on the slit of a Hilger E3 quartz spectrograph. As usual, the resonance radiation from the scattered light was effectively suppressed by a mercury vapour filter. Using Ilford Special Rapid plates and a slitwidth of 0·035 mm., exposures of the order of three hours were sufficient to get a spectrogram which exhibited all the features. Photographs were taken with exposures of the order of one day; but they did not exhibit any new features. It was noticed that, due to prolonged exposure, the crystal got slightly coloured. Hence, while taking long exposure photographs, fresh crystals were used every three hours. In order to exhibit the doublet nature of some of the Raman lines more clearly, lightly exposed photographs were also taken using a fine slit (0·02 mm.).

3. RESULTS

As is evident from the photographs reproduced in Fig. 1, the Raman spectrum of sodium chlorate consists of a series of sharply defined Raman lines, the frequency shifts of which are entered in Table I. The sharpness of the lines is more clearly seen in the microphotometric record reproduced in Fig. 2. The figures given in brackets against the frequency shifts in Table I represent visual estimates of the relative intensities of the lines. The values

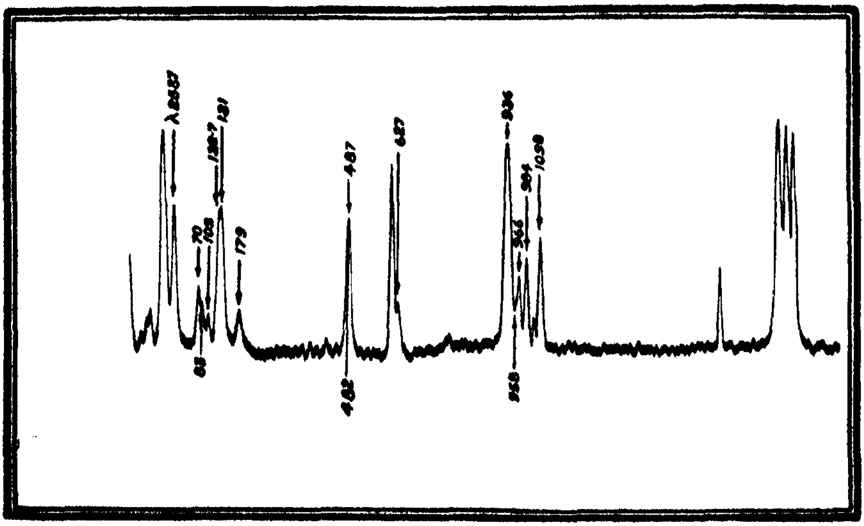

FIG. 2. Microphotometric Record of Raman Spectrum of Sodium Chlorate.

TABLE I

Raman Spectrum of Sodium Chlorate

Internal Oscillations				Lattice Oscillations			
Author		Rousset, Laval and Lochet (1943)		Author		Rousset, Laval and Lochet (1943)	
482 487	[10]	482 487	[6]	70	[6]		
				83	[4]		
627	[4]	625	[3]				
..		665	[1]	103	[2]		
..		925	[0]				
933 936	[20]	933 936	[10]	122·7 131	[15]	122·5 131	[3]
959 966	[3] [5]	963 966	[27]	179	[4]	179	[0]
984	[6]	984	[5]				
..		1003	[0]				
1028	[8]	1025	[5]				
		1285	[0]				

of the frequency shifts of the Raman lines of sodium chlorate recorded by Rousset, Laval and Lochet are included in the same table. The author's results agree reasonably well with those reported by Rousset, Laval and Lochet.

The spectrum recorded by the author exhibits nine frequency shifts due to the internal oscillations of the chlorate ion as compared to thirteen observed by Rousset, Laval and Lochet. The existence of lines of negligible intensity namely, 665, 925, 1003 and 1285 cm.$^{-1}$ reported by Rousset, Laval and Lochet could not be confirmed. Of these, the line at 1003 cm.$^{-1}$, even if present, cannot be identified in the present case, as it would fall adjacent to the mercury line λ 2603·2. In agreement with their observations, the doublet nature of the lines 482–87, 933–36 and 959–66 can be clearly seen in the enlarged photograph reproduced in Fig. 3. As compared with three lattice lines reported by Rousset, Laval and Lochet, the spectrum recorded here exhibits not less than six lattice lines of which the doublet 122·7–131 cm.$^{-1}$ (Fig. 3) is the most intense one. The line 179 cm.$^{-1}$ is rather broad.

4. DISCUSSION

Sodium chlorate crystallises in the cubic tetrahedral class. Zachariasen has shown by X-ray analysis that there are four molecules of sodium chlorate in the unit cell (Wyckoff, 1931). They are so arranged as to give the crystal rotatory power. Each molecule consists of three oxygen atoms arranged in the form of an equilateral triangle with a separation of 2·38 A between the oxygen centres. The chlorine atom is located at a distance of 0·48 A above the plane of the oxygen atoms in a line through their centre of gravity. The sodium atom lies above the chlorine at a distance of 6·12 A. as in Fig. 4. The O–Cl distance is 1·476 A.

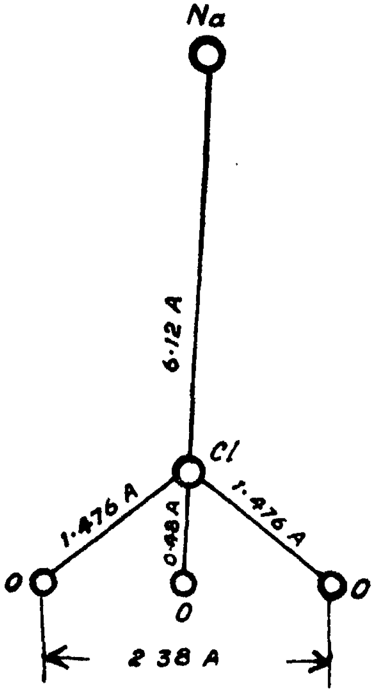

FIG. 4. Structure of $NaClO_3$ Molecule.

On semi-theoretical grounds and later, by quantum mechanical considerations it has been shown by Zachariasen that the chlorate ion in the free state has a pyramidal structure of point group C_{3v}. This has been confirmed by Venkateswaran and Shen, Yao and Wu by experimental studies. Such a unit possesses two totally symmetric vibrations ν_1 and ν_3 and two doubly degenerate vibrations ν_2 and ν_4, all of which are active in Raman effect. The four frequency shifts observed with solutions, namely, 930, 975, 615 and 479 cm.$^{-1}$ have been identified as ν_1, ν_2, ν_3 and ν_4 respectively.

Measurements on the Faraday effect in sodium chlorate by Ramaseshan (1948) indicate that the bond between Na and Cl atoms in the crystalline state is more of a covalent type than of ionic type. On the basis of this, the sodium chlorate molecule should belong to the symmetric class C_{3v}. such a molecule will have 3 vibrations which are symmetric with respect to the axis, called parallel vibrations and 3 perpendicular vibrations, namely, ν_1, ν_3, and ν_5, and ν_2, ν_4 and ν_6 respectively. The latter vibrations are doubly degenerate. These vibrations are graphically represented in Fig. 5. As the interaction between Na and o atoms is negligible, ν_1 of the NaClO$_3$ molecule is approximately the valence vibration ν_1 of the free ClO$_3$-ion (930 cm.$^{-1}$); ν_3 will correspond to the deformation vibration ν_3 of the free ClO$_3$-ion (615 cm.$^{-1}$) and ν_5 is the group movement of ClO$_3$ ion against Na. Of the three perpendicular vibrations, ν_2 and ν_4 correspond respectively to the valence vibration ν_2 (975 cm.$^{-1}$) and the deformation vibration ν_4 (479 cm.$^{-1}$) of the free ClO$_3^-$ ion. ν_6 is the vibration of the chlorine atom with respect to the rest of the molecule, perpendicular to the symmetry axis. Comparing the frequencies observed in crystalline sodium chlorate with those of the ClO$_3$ ion, it is possible to give the following assignments.

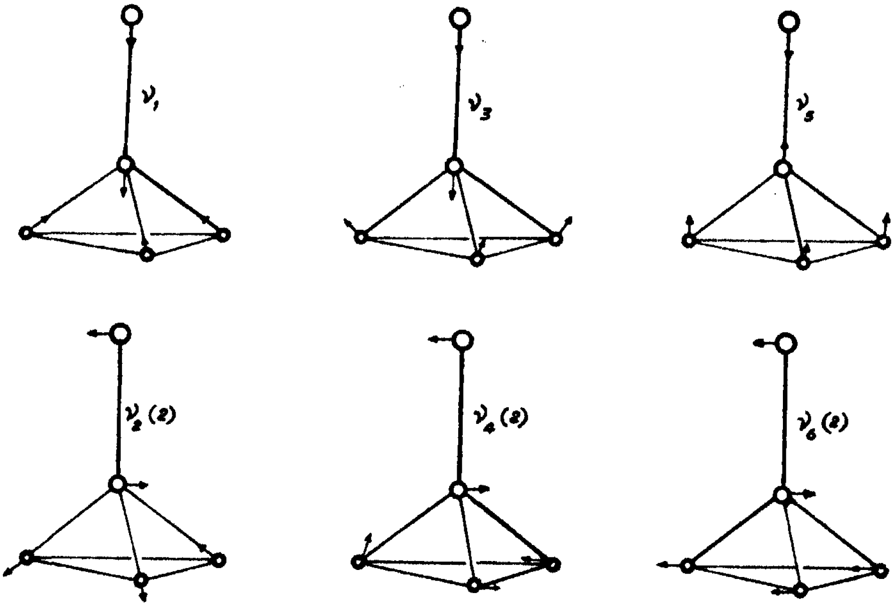

FIG. 5. The different modes of vibrations of the NaClO$_3$ Molecule.

ν_1	933–36 cm.$^{-1}$	ν_2	966 and 984 cm.$^{-1}$
ν_3	627 cm.$^{-1}$	ν_4	482–487 cm.$^{-1}$
ν_4	959 cm.$^{-1}$	ν_6	1028 cm.$^{-1}$

As is to be expected, because of the lower symmetry of NaClO$_3$ molecule in the lattice, the degeneracies of ν_2 and ν_4 of the free NaClO$_3$ molecule are removed and appear as double lines. The doubling of the principal frequency ν_1 (933–36 cm.$^{-1}$) may be attributed to the fact that there are four molecules in the unit cell.

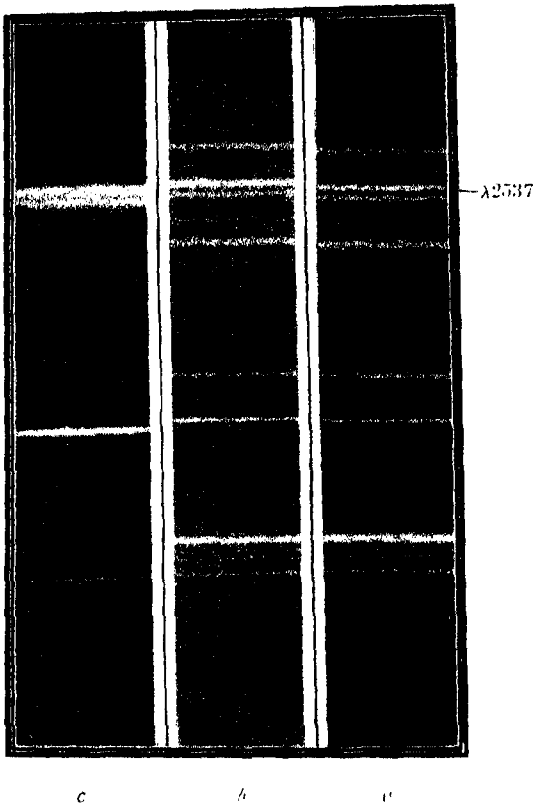

Fig. 1. *a* Raman spectrum of sodium chlorate (heavily exposed)

b ,, ,, (light picture)

c Mercury spectrum

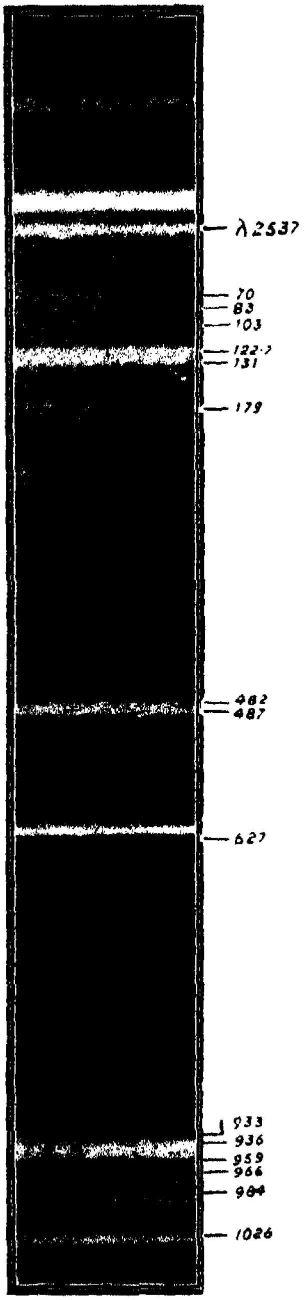

Fig. 3. Raman spectrum of sodium chlorate (taken with E3 quartz-spectrograph)

The six lattice lines observed in the spectrum of sodium chlorate crystal are due to the external oscillations. These external oscillations are both of the rotatory type and the translatory type and there will be some interaction between the two. As the translatory type of oscillations are likely to be of low frequencies and low intensities, the lines 70, 83 and 103 cm.$^{-1}$ may come under this class. The rotatory type of oscillations will result in intense Raman lines especially if the rotatory groups are strongly optically anisotropic. The intense doublet 122·7–131 cm.$^{-1}$ and the line at 179 cm.$^{-1}$ observed in the spectrum may be assigned to oscillations of the rotatory type.

In conclusion, the author desires to record her grateful thanks to Prof. R. S. Krishnan for his valuable guidance and encouragement in the present work.

5. SUMMARY

The Raman spectrum of sodium chlorate in the form of single crystal has been studied using λ 2537 radiation for excitation. The recorded spectrum exhibits nine Raman lines due to internal oscillations and six lines due to lattice oscillations, of which three lattice lines 70, 83 and 103 cm.$^{-1}$ are recorded for the first time by the author. Assignments have been given to all the fifteen Raman lines.

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DER EINFLUSS DES KATIONS AUF DIE INTENSITÄT DES RAMANSPEKTRUMS VON SALZPULVERN

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Synopsis.—Der Ausdruck $\delta\alpha/\delta q$, der die Abhängigkeit der Polarisierbarkeit von der Normalkoordinate einer Molekülschwingung beschreibt, wird nach der wellenmechanischen Störungsrechnung mit Hilfe eines Variationsprinzips behandelt. Es ergibt sich dabei eine Formel, die das Verhalten von $\partial\alpha/\partial q$ in starken Feldern erkennen läßt:

$$\partial\alpha/\partial q = \partial\alpha_0/\partial q\cdot(1 - kf^2)$$

Der Index Null bezieht sich auf die Feldstärke $f = 0$. Die Formel enthält ein "Verfestigungsglied" kf^2, das die Abnahme von $\partial\alpha/\partial q$ mit wachsender Feldstärke zum Ausdruck bringt. Der Proportionalitätsfaktor k hängt von der Polarisierbarkeit des unverzerrten Moleküls ab. Die Abnahme kann bei den großen Feldstärken innerhalb von Ionenkristallen bis 50% des Grenzwertes, den $\partial\alpha/\partial q$ bei unendlich kleiner Feldstärke annimmt, betragen. Angewandt auf das Ramanspektrum von Salzpulvern bedeutet dies, daß die Intensität des Ramanspektrums bei gleichbleibendem komplexen Anion mit wachsendem Ionenpotential des Kations abnimmt. Dies wird durch das Experiment im großen und ganzen bestätigt.

1. Einleitung

Im Physikalischen Institut der Technischen Hochschule Graz wurden in den letzten Jahren die Ramanspektren zahlreicher kristallisierter organischer und anorganischer Salze in Pulverform aufgenommen. Die Streufähigkeit im Ramaneffekt ist bei diesen Salzen sehr verschieden. Dies liegt zum Teil an wechselnden Versuchsbedingungen wie z.B. Korngröße und Fluoreszenz. Es scheint aber auch ein systematischer Kationeneinfluß zu bestehen dergestalt, daß in kristallisierten Salzen die Intensität der Ramanstreuung eines komplexen Anions mit wachsendem Ionenpotential der umgebenden Kationen abnimmt.

2. Problemstellung

Nach der Polarisierbarkeitstheorie von *G. Placzek*[1] ist die Intensität einer Ramanlinie gegeben durch:

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[1] *G. Placzek*, Handbuch der Radiologie IV / 2. Leipzig, 1934.

$I \sim \left(\frac{\partial \alpha}{\partial q}\right)^2$ $\alpha =$ Polarisierbarkeit

$q =$ Normalkoordinate der Molekülschwingung

Angeregt durch den eingangs beschriebenen, experimentell allerdings recht wenig gesicherten Befund, ist es das Ziel dieser Arbeit zu zeigen, daß $\partial \alpha / \partial q$ und damit die Streufähigkeit im Ramaneffekt mit wachsendem Ionenpotential der Kationen merklich abnimmt.

Eine derartige Abnahme ist von der Polarisierbarkeit selbst schon seit langem bekannt.[2] Sie läßt sich auch quantenmechanisch erklären.[3] Die folgende Untersuchung wird zeigen, daß nach der Quantenmechanik auch $\partial \alpha / \partial q$ eine Funktion der Feldstärke ist und aus dem gleichen Grunde mit wachsender Feldstärke abnimmt wie α.

3. ALLGEMEINE BEMERKUNGEN ÜBER DIE BERECHNUNG DER POLARISIERBARKEIT UND DIE WELLENMECHANISCHE STÖRUNGSRECHNUNG

Das Verhalten von $\partial \alpha / \partial q$ in starken Feldern läßt sich ziemlich leicht überblicken, wenn man eine von *H. Hellmann*[3] angegebene Formel für die Polarisierbarkeit des H-Atoms nach q differenziert. Es ergibt sich dabei unmittelbar, daß $\partial \alpha / \partial q$, wie schon gesagt, genauso mit der Feldstärke abnimmt wie α.

Die Formel von *Hellmann* ist jedoch in der mir zugänglichen Literatur nicht so abgeleitet, daß man sie für Probleme der Lichtstreuung ohneweiters verwenden kann, da die Polarisierbarkeit nicht durch das induzierte Dipolmoment, sondern durch die Polarisationsenergie definiert ist. Es läßt sich auch der Einfluß gewisser Näherungen und der Zusammenhang zwischen α und q nicht überblicken.

Es erschien mir daher notwendig, die bekannten Ergebnisse für die Polarisierbarkeit, in einer für das vorliegende Thema geeigneten Form neu abzuleiten und sie erst dann auf den noch nicht behandelten Ausdruck $\partial \alpha / \partial q$ anzuwenden.

Im allgemeinen wird die Polarisierbarkeit eines Atoms oder Moleküls so ermittelt, daß man nach den Methoden der wellenmechanischen Störungsrechnung das durch ein äußeres elektrisches Feld f induzierte Dipolmoment μ berechnet. Daraus findet man α mit Hilfe der Definitionsgleichung: $\mu = \alpha f$.

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[2] *K. Fajans* u. *G. Joos*, Z. Physik, 23, 1 (1924).

[3] *H. Hellmann*, Einführung in die Quantenchemie, Leipzig, 1937.

Ich werde zur Berechnung von α in dieser Arbeit ein Variationsverfahren der Störungsrechnung verwenden. Dies wird wahrscheinlich allen denen, die die wellenmechanische Behandlung des Ramaneffektes kennen, als eigenartiger Umweg erscheinen. Denn für die allgemeine Theorie des Ramaneffektes ist es wesentlich, jene Form der Störungsrechnung anzuwenden, bei der die gestörte Eigenfunktion nach den Eigenfunktionen des ungestörten Systems entwickelt wird. Nur bei diesem Verfahren treten die für alle Wechselwirkungen zwischen Licht und Materie so wichtigen Übergangsfrequenzen ν_{ik} des Systems in Erscheinung. Beim Schwingungsramaneffekt ist es zwar erlaubt, gewisse Ausdrücke, die sich auf die Elektronenhülle beziehen, zur makroskopischen Polarisierbarkeit zusammenzufassen; trotzdem bedeutet es eine gewisse Sinnwidrigkeit dieses α, das schon eine ganz bestimmte, auf die Lichtstreuung besonders zugeschnittene, quantenmechanische Gestalt besitzt, nun mit Hilfe einer anderen Form der Störungsrechnung, z.B. mit Hilfe eines Variationsverfahrens, neu zu bestimmen. Dieser Vorgang kann nur durch seine mathematische Zweckmäßigkeit entschuldigt werden Er gestattet es, die fehlende Kenntnis der Eigenwerte und Eigenfunktionen des ungestörten Systems durch ein Variationsprinzip zu ersetzen. Dies ist folgendermaßen gemeint:

Die gestörte ψ-Funktion eines Systems läßt sich immer darstellen als Produkt der ungestörten Eigenfunktion mit einem Störfaktor:

$$\psi = \psi_0 (1 + v).$$

Für v ergibt sich bei Entwicklung nach Eigenfunktionen:

$$v = \frac{1}{\psi_0} \Sigma' \frac{\int \psi_n^* \, u \, \psi_0 \, d\tau}{E_0 - E_n} \cdot \psi_n$$

ψ_n und E_n sind die meist unbekannten Eigenwerte und Eigenfunktionen des ungestörten Systems.

Man kann v aber auch so bestimmen, daß man den Mittelwert der Energie

$$\bar{H} = \frac{\int \psi^* H_{op} \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \bar{H}_0 + \bar{H}_1$$

zu einem Minimum macht.

$H_{op} = H_{op,o} + u$ bedeutet den gestörten Energieoperator; u ist das Störpotential, $\bar{H}_1$ die mittlere Eigenwertstörung.

Der Strich über einer Größe bedeutet Mittelwertbildung, z.B.

$$\bar{u} = \frac{\int \psi^* u \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

Die Minimumsbedingung läßt sich auch in einer anderen, für die Variation bequemeren Fassung anschreiben, deren etwas umständliche Ableitung hier nicht angegeben wird (*loc. cit.* 3). Sie lautet:

$$\bar{H}_1 = \frac{\bar{u} + 2\overline{uv} - 2\bar{u}\bar{v} + \overline{uv^2} - \bar{u}\overline{v^2} + \frac{ae^2}{2}\,\overline{(\mathrm{grad}\ v)^2}}{1 + 2\bar{v} + \overline{v^2}} \tag{1}$$

$$(\mathrm{grad}\ v)^2 = \sum_{i=1}^{3N} \left(\frac{\partial v}{\partial x_i}\right)^2$$

a = Radius des H-Atoms

e = elektrisches Elementarquantum

x_i = Lagekoordinaten aller zum System gehörigen Partikel.

Wählt man nun v so, daß H_1 ein Minimum wird, dann ist dieses v das für das betreffende Störungsproblem richtige Störglied. Es ergibt sich als Funktion nur bekannter Größen und zwar der Koordinaten, der ungestörten Eigenfunktion und des Störpotentials u.

Der Störfaktor $(1 + v)$ hat einr ziemlich anschauliche Bedeutung. Sein Quadrat beschreibt z.B. im Fall der Elektroneneigenfunktion eines Moleküls die Verzerrung, die die Ladungswolke durch die Störung erleidet.

4. DIE POLARISIERBARKEIT DES H-ATOMS

Da die Berechnung der Polarisierbarkeit mit Hilfe des Variationsprinzipes der Störungsrechnung zu einem Spezialgebiet gehört, das den meisten Lesern nicht geläufig sein dürfte, werde ich das Verfahren zuerst für den einfachsten Fall, das Wasserstoffatom, erläutern.

Zunächst müssen alle in Formel (1) auftretenden Größen festgesetzt werden.

Legt man die z-Achse eines an sich willkürlichen, kartesischen Koordinatensystems in die Richtung eines homogenen elektrischen Feldes f und den Koordinatenursprung in den Kern des H-Atoms, dann wird das Störpotential an der Stelle z

$$u = efz;$$

denn diese Energie wird frei wenn man ein Elektron von einer Stelle $z = 0$ im Feld nach z verschiebt.

v setzt man in erster Näherung an:

$$v = \lambda z$$

λ ist eine Konstante, die erst durch Minimisieren der Eigenwertstörung $\bar{H}_1$ bestimmt wird.

Man wählt diesen Ansatz deshalb, weil v, wie schon gesagt, im wesentlichen die durch die Störung bedingte Deformation der Ladungswolke beschreiben soll. Diese Deformation wird im homogenen Feld, zumindest in erster Näherung, nur in der z-Richtung erfolgen. Will man den Absolutwert der Polarisierbarkeit genauer ermitteln, dann muß man für v einen Ansatz mit mehreren Variationsparametern machen, z.B. $v = \lambda z (1 + \sigma r)$. Eine solche hohe Näherung ist jedoch im Rahmen dieser Arbeit nicht notwendig, da nur ein allgemeiner Überblick über das Verhalten der Ableitung $\partial\sigma/\partial q$ in starken Feldern gewonnen werden soll.

Mit obigen Ansätzen für u and v vereinfacht sich Formel (1) wesentlich, da wegen der Kugelsymmetrie des Wasserstoff-Grundzustandes alle Ausdrücke mit ungeraden Potenzen von z bei der Mittelwertsbildung verschwinden. Man erhält:

$$\overline{H}_1 = \frac{2\overline{uv} + \frac{ae^2}{2}\overline{(\text{grad } v)^2}}{1 + \overline{v^2}}. \tag{2}$$

Für die Mittelwerte findet man:

$$\overline{uv} = \lambda e f \overline{z^2}, \quad \overline{v^2} = \lambda^2 \overline{z^2}, \quad \overline{(\text{grad } v)^2} = \overline{(\partial v/\partial z)^2} = \lambda^2.$$

Damit wird aus (2):

$$\overline{H}_1(\lambda) = \frac{2\lambda e f \overline{z^2} + \frac{ae^2}{2}\lambda^2}{1 + \lambda^2 \overline{z^2}} \tag{3}$$

Differenzieren nach λ und Nullsetzen des Differential-quotienten $\partial\overline{H}_1(\lambda)/\partial\lambda$ liefert entsprechend dem früher besprochenen Variationsprinzip die richtigen Werte für λ:

$$\frac{\partial \overline{H}_1(\lambda)}{\partial\lambda} = (1 + \lambda^2\overline{z^2})(2ef\overline{z^2} + ae^2\lambda) - \left(2\lambda e f \overline{z^2} + \frac{ae^2}{2}\lambda^2\right) 2\lambda \overline{z^2} = 0.$$

Durch Ausmultiplizieren und Ordnen nach Potenzen von λ erhält man:

$$2ef\overline{z^2}\lambda^2 - ae^2\lambda - 2cf\overline{z^2} = 0$$

$$\lambda_{1,2} = \frac{ae^2}{4ef(\overline{z^2})^2}\left(1 \pm \sqrt{1 + \frac{16 f^2 (\overline{z^2})^3}{a^2 e^2}}\right)$$

Der Ausdruck $16 f^2 (\overline{z^2})^3 / a^2 e^2$ unter der Wurzel ist in allen praktischen Fällen klein gegen 1. Dies erkennt man, wenn man z.B. für f jene Feldstärke einsetzt, die durch ein einfach geladenes positives Ion im Abstand $4a \sim 2$ Å hervorgerufen wird: $f^2 = e^2/16^2 a^4$ und bedenkt, daß im Fall des H-Atoms $\overline{z^2}$ definitionsgemäß identisch a^2 ist. Der Ausdruck unter der Wurzel wird dann $1 + 1/16$. Man kann die Wurzel daher nach der binomischen Reihe entwickeln und die Reihe nach dem 3. Glied abbrechen und findet dann für λ:

$$\lambda_{1,2} = \frac{ae^2}{4ef(\overline{z^2})^2}\left[1 \pm \left(1 + \frac{8 f^2 (\overline{z^2})^3}{a^2 e^2} - \frac{32 f^4 (\overline{z^2})^6}{a^4 e^4}\right)\right]$$

Von den beiden Ausdrücken für λ führt nur der mit negativem Vorzeichen vor der runden Klammer zu einer physikalisch sinnvollen Lösung, da bei positivem Vorzeichen λ unendlich wird, wenn f gegen Null geht.

Die Lösung des Variationsproblems lautet also:

$$\lambda = -\frac{2f\overline{z^2}}{ae} + \frac{8f^3(\overline{z^2})^4}{a^3e^3}. \tag{4}$$

Damit läßt sich der Mittelwert des induzierten Diplomomentes leicht berechnen:

$$\bar{\mu} = e\int z\psi^*\psi\,d\tau = e\int z(1+v)^2\psi_0{}^*\psi_0 d\tau. \tag{5}$$

Setzt man für $v = \lambda z$ aus Formel (4) ein und berücksichtight man, daß Ausdrücke mit ungeraden Potenzen von z wegen der Kugelsymmetrie von $\psi_0{}^*\psi_0$ bei der Mittelwertbildung wegfallen, dann wird:

$$\mu = \frac{4(\overline{z^2})^2}{a}f - \frac{16(\overline{z^2})^5}{a^3e^2}f^3 = \alpha f$$

$$\alpha = \frac{4(\overline{z^2})^2}{a} - \frac{16(\overline{z^2})^5}{a^3e^2}f^2$$

Dies läßt sich in übersichtlicher Weise schreiben:

$$\alpha = \alpha_0\left(1 - \frac{f^2\,\alpha_0{}^{3/2}}{2a^{1/2}e^2}\right) \tag{6}^*$$

$\alpha_0 = \left(\frac{4(\overline{z^2})^2}{a}\right)$ ist der Grenzwert der Polarisierbarkeit, wenn f gegen Null geht.

Das im Rahmen dieser Untersuchung wichtigste Ergebnis der Rechnung, ist die Abhängigkeit der Polarisierbarkeit von der Feldstärke f. Die Polarisierbarkeit zeigt bei großer Feldstärke Verfestigungserscheinungen, d.h. sie nimmt mit dem Quadrat der Feldstärke ab und zwar umso mehr, je größer α_0 ist. Es ist leicht abzuschätzen, daß bei Feldsterken, wie sie an den Ionenschwerpunkten in kristallisierten Salzen auftreten, die Abnahme der Polarisierbarkeit bis 50% betragen kann. Dies erkennt man, wenn man z.B. für f etwa $3e/16a^2$ und für α_0 die Polarisierbarkeit des Iod-ions einsetzt ($\alpha_{J^-} \simeq 64a^3$).

Wenn man die oben gefundenen Ergebnisse für Probleme der Lichtstreuung und Brechung an Kristallen heranzieht, dann muß man bedenken, daß die induzierende Feldstärke aus zwei Teilen besteht. Aus dem schwachen Feld f_1 des Lichtes und aus dem starken Feld f_2 der Ionen. Wäre das elektrische Feld des

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[*] Diese Formel läßt sich viel einfacher ableiten, wenn man α durch die Polarisationsenergie $H_1 = \frac{\alpha}{2}f^2$ definiert. Da für das Problem der Ramanstreuung aber vor allem das induzierte Dipolmoment interessiert, war obige etwas komplizierte Ableitung angemessen.

Lichtes statisch, dann brauchte man in den Formeln (4-6) bloß f durch $(f_1 + f_2)$ ersetzen, ohne sonst an dem Resultat irgend etwas zu ändern. Im elektrischen Wechselfeld liegen die Dinge nicht so einfach. Man könnte z.B. annehmen, daß der Verfestigungseffekt nur bei jener Phase der elektromagnetischen Schwingung voll zur Wirkung kommt, bei der Ionen—und Lichtfeld gleichgerichtet sind. Der durchschnittliche Verfestigungseffekt wäre dann im Wechselfeld geringer als im statischen Feld. Ich möchte jedoch auf diese undurchsichtigen Verhältnisse hier nicht näher eingehen.

5. DIE POLARISIERBARKEIT EINES BELIEBIGEN MOLEKÜLS

In diesem Kapitel soll untersucht werden, wie weit die für das H-Atom abgeleiteten Ergebnisse auch für beliebige Moleküle gelten. Es wird sich zeigen, daß die Polarisierbarkeit α eines Moleküls im wesentlichen mit der gleichen Näherung als Summe der von den einzelnen Elektronen herrührenden Polarisierbarkeitsanteile α_e dargestellt werden darf, mit der es erlaubt ist die Eigenfunktion ψ des ganzen Moleküls als Produkt der einzelnen Elektroneneigenfunktionen ψ_e anzusetzen, wobei jedes einzelne ψ_e nur von den Koordinaten des e-ten Elektrons abhängen darf.

Nach *Hellmann* darf man diesen Ansatz ohne einen großen Fehler zu begehen dann machen, wenn sich die Elektronen des Moleküls in Gruppen ungefähr gleich stark gebundener Elektronen einteilen lassen, innerhalb derer die einzelnen Elektronenspins nicht parallel sind. Der Anteil der um eine Grössenordnung fester gebundenen Rumpfelektronen an der Polarisierbarkeit werde vernachlässigt. Dann kommen als Gruppen ähnlicher Bindefestigkeit nur die Valenzelektronen in Frage, von denen sowohl die nicht-anteiligen, als auch die anteiligen der homöopolaren Bindung in Paaren mit antiparallelem Spin auftreten.

Ich werde mich daher im Folgenden nur auf die Behandlung der Polarisierbarkeit von einfachen homöopolaren Bindungen beschränken, doch möchte ich schon hier bemerken—eine ausführlichere Kritik folgt am Schluß—, daß die hier vor allem interessierenden Verfestigungseffekte auch dann immer auftreten, wenn der einfache Produktansatz nicht mehr erlaubt ist und der Absolutwert der Polarisierbarkeit daher nicht mehr so einfach ermittelt werden kann.

Die Berechnung verläuft wie folgt:

Man geht wieder von der allgemeinen Formel (1) aus, legt die Werte für u und v fest und macht die mittlere Eigenwertstörung $\bar{H}_1$ durch Variation der Konstanten zu einem Minimum. u ergibt sich dabei eindeutig aus dem betreffenden Störungsproblem, während für v ein Ansatz gemacht werden muß, der geeignet ist die Deformation der Ladungswolke passend zu beschreiben.

Mit dem Index e für die Elektronen und a für die Atomkerne wird das Störpotential:

$$u = ef\left(\sum_e z_e - \sum_a N_a z_a\right) \qquad (N_a = \text{Kernladung}),$$

worin e über alle Elektronen und a über alle Kerne läuft. Die z-Koordinate wurde willkürlich in die Richtung des Feldes gelegt.

Die von den Kernen abhängigen Anteile von u sind Konstante bezüglich der Mittelwertsbildung mit der Elektroneneigenfunktion und fallen daher in der Gleichung (1) heraus. Die Invarianz von Gleichung (1) gegenüber Hinzufügen beliebiger Konstanten zu u gestattet es auch, den Koordinatenursprung für jede Schale des Moleküls, also auch für die von uns betrachtete Schale einer einfachen homöopolaren Bindung, in den Schwerpunkt der zugehörigen Ladungsverteilung zu legen. Dadurch wird Formel (1) wesentlich vereinfacht, weil alle Glieder, die $\bar{u}$ enthalten, herausfallen.

Für v setzt man wieder:

$$v = \sum_e \lambda_e z_e$$

Für die Mittelwerte erhält man wegen des Produktansatzes

$$\psi = \psi_1 \cdot \psi_2 \ldots . \psi_e$$

$$\overline{uv} = ef \sum_{ek} \lambda_e \overline{z_e z_k} = ef \sum_e \lambda_e \overline{z_e^2}, \qquad \overline{v^2} = \sum_{ek} \lambda_e \lambda_k \overline{z_e z_k} = \sum_e \lambda_e^2 \overline{z_e^2}$$

$$\overline{(\operatorname{grad} v)^2} = \sum_e \overline{\left(\frac{\partial v}{\partial z_e}\right)^2} = \sum_e \lambda_e^2$$

$\overline{uv^2}$ enthält nur Glieder mit $\overline{z_e^3}$: Wegen der Verlegung des Koordinatenursprunges in den negativen Ladungsschwerpunkt wird auch im allgemeinsten Fall von Elektronenschalen ohne Symmetrieebene senkrecht zur Feldrichtung $\overline{uv^2}$ so klein, daß man es mit dem gleichen Recht wie die Wechselwirkung zwischen den einzelnen Elektronenschalen des Moleküls vernachlässigen kann. Die Berechnung von α läßt sich übrigens in einer höheren Näherung auch mit Berücksichtigung von $\overline{uv^2}$ durchführen, doch wird dabei der Gang der Rechnung unübersichtlich kompliziert, ohne am Ergebnis bezüglich des Verfestigungseffektes etwas Wesentliches zu ändern.

Mit obigen Werten für die Mittelwerte erhält man als Eigenwertstörung:

$$\overline{H}_1(\lambda_e) = \frac{2ef \sum_e \lambda_e \overline{z_e^2} + \frac{\alpha e^2}{2} \sum_e \lambda_e^2}{1 + \sum_e \lambda_e^2 \overline{z_e^2}}$$

Durch partielles Differenzieren nach den λ_e und Nullsetzen der Ableitungen erhält man e Gleichungen für die λ_e:

$$\frac{\partial \overline{H}_1(\lambda_k)}{\partial \lambda_k} = (1 + \lambda_k^2 \overline{z_k^2} + \sum_e{}' \lambda_e^2 \overline{z_e^2})(2ef\overline{z_k^2} + ae^2\lambda_k) -$$
$$- (2ef\,\lambda_k \overline{z_k^2} + 2ef \sum_e{}' \lambda_e \overline{z_e^2} - \frac{ae^2}{2}\lambda_k^2 - \frac{ae^2}{2}\sum_e{}' \lambda_e^2)\, 2\lambda_k \overline{z_k^2}.$$

Der Strich am Summenzeichen bedeutet, daß über den Index k nicht mehr summiert wird.

Durch Ausmultiplizieren und Ordnen nach Potenzen von λ_k erhält man näherungsweise:

$$2ef\overline{z_k^2}\lambda_k^2 - \lambda_k(ae^2 - 4efz_k^2 \sum_e{}' \lambda_e \overline{z_e^2}) - 2ef\overline{z_k^2} = 0.$$

Damit wird

$$\lambda_k = \frac{ae^2}{4ef(z_k^2)^2}\left(1 - \frac{4ef\overline{z_k^2}\sum_e{}' \lambda_e \overline{z_e^2}}{ae^2} \pm \sqrt{1 - \frac{8efz_k^2 \sum_e{}' \lambda_e z_e^2}{ae^2} + \frac{16f^2(z_k^2)^3}{a^2e^2}}\right)$$

Berücksichtigt man wieder nur die Lösung mit negativer Wurzel und entwickelt man die Wurzel bis zum dritten Glied der binomischen Reihe, dann findet man:

$$\lambda_k = -\frac{2f\overline{z_k^2}}{ae}\left[1 + \frac{(\sum_e{}' \lambda_e^2 \overline{z_e^2})^2}{z_k^2}\right] + \frac{8f^3(\overline{z_k^2})^4}{a^3e^3} \tag{7}$$

Setzt man die eckige Klammer näherungsweise gleich 1, was wegen der Kleinheit der λ_e in Rahmen der schon durchgeführten Näherungen ohneweiters erlaubt ist, dann erhält man für λ_k und damit für alle λ_e die gleiche Formel, die schon beim Wasserstoffatom abgeleitet wurde.

Das induzierte Dipolmoment errechnet sich nun ganz einfach. Wegen des Produktansatzes $\psi = \psi_1 \cdot \psi_2 \ldots . \psi_e$ wird

$$\mu = e\int \sum_e z_e(1 + z_e\lambda_e)^2 \psi_e^* \psi_e d\tau_e = e\int \sum_e (z_e + 2z_e^2\lambda_e + z_e^3\lambda_e^2)\psi_e^*\psi_e d\tau_e.$$

Infolge der schon mehrfach beschriebenen Wahl des Koordinatenursprunges verschwindet das Integral über z_e exakt und das über $z_e^3\lambda_e^2$ näherungsweise und es gilt:

$$\mu = e\int \sum_e 2z_0^2 \lambda_e \psi_e^* \psi_e d\tau = \sum_e 2\lambda_e \overline{z_e^2} = \sum_e \mu_e. \tag{8}$$

Nach Formel (8) läßt sich das in beliebigen Molekülen induzierte Dipolmoment und damit auch die Polarisierbarkeit additiv aus Anteilen der einzelnen Elektronen zusammensetzen, allerdings nur dann, wenn ein Produktansatz für die Eigenfunktion erlaubt ist, wie z. B. bei den Bindungselektronen einer einfachen homöopolaren Bindung.

Man sieht in diesem Fall unmittelbar, daß die hier vor allem interessierenden Verfestigungseffekte auch bei beliebigen Molekülen und beliebigen Elektronenschalen, z.B. auch bei den für die Ramanstreuung maßgebenden Bindungselektronen auftreten, da die λ_e in Formel (8) nach (7) die gleiche Abhängigkeit von der Feldstärke zeigen wie beim H-Atom.

Ist der Produktansatz nicht mehr angebracht, dann werden zwar die in der Rechnung auftretenden Mittelwerte kompliziertere Ausdrücke; die allgemeine Form der Lösung für die λ_e und damit die Verfestigungseffekte bleiben jedoch erhalten, da letztere unabhängig vom Einzelproblem im wesentlichen mit dem Nenner der allgemeinen Störformel (1) zusammenhängen.

6. QUANTENMECHANISCHE BEHANDLUNG DES AUSDRUCKES $\partial\alpha/\partial q$

Im vorigen Kapitel wurde gezeigt, daß sich die Polarisierbarkeit eines beliebigen Moleküles bzw. einer homöopolaren Einfachbindung, näherungsweise als Summe von Elektronenanteilen darstellen läßt, für die einzeln Formel (6) gilt. Ich werde daher im Folgenden die beim H-Atom abgeleiteten Formeln für λ und α verwenden und den Elektronenindex e und die Summierung über alle e weglassen, ohne Rücksicht darauf, wieviel Elektronen das behandelte System besitzt.

Das eigentliche Problem dieser Arbeit, die Frage ob auch der Ausdruck $\partial\alpha/\partial q$ Verfestigungserscheinungen zeigt, ist nun sehr einfach zu lösen.

Wenn man überhaupt annimmt, daß α eine Funktion der Normalkoordinate q ist, dann ist in Formel (6) α_0 die *einzige* Größe, die von q abhängig sein kann. Damit ergibt sich für die Ableitung nach q:

$$\frac{\partial\alpha}{\partial q}=\frac{\partial\alpha_0}{\partial q}-\frac{5f^2\alpha_0^{3/2}}{4a^{1/2}e^2}\frac{\partial\alpha_0}{\partial q}=\frac{\partial\alpha_0}{\partial q}\left(1-\frac{5f^2\alpha_0^{3/2}}{4a^{1/2}e^2}\right) \tag{9}$$

$\partial\alpha/\partial q$ zeigt also bis auf einen Zahlenfaktor die gleichen Verfestigungserscheinungen wie α.

Die Begründung dieser Behauptung durch einfache Differentiation von Formel (6) ist zwar, wie sich zeigen wird, ziemlich korrekt, doch nicht sehr befriedigend, da nichts über den Mechanismus des Zusammenhanges zwischen α und q ausgesagt wird und der Verdacht besteht, das Ergebnis könnte anders ausfallen, wenn man α nicht als Funktion von α_0 ausdrückt, sondern entsprechend der Ableitung, unmittelbar als Funktion von λ und $\bar{r}_\nu$ die beide von q abhängen können.

Ich werde daher zum Abschluß Formel (9) auf korrektere und physikalisch durchsichtigere Weise ableiten, auch auf die Gefahr hin, den Leser durch die etwas umständlichen Rechnungen noch weiter zu ermüden.

Behandelt man die Verzerrungen des schwingenden Moleküls als Störung des ruhenden Moleküls, dann kann man die durch die Verzerrung gestörte Elektroneneigenfunktion nach dem Variationsprinzip darstellen als:

$$\psi = \psi_0 (1 + \epsilon q)$$

ϵ ist ein Variationsparameter, der auf alle Fälle klein gegen 1 ist und nur bei einer Absolutberechnung von $\partial a/\partial q$ interessieren würde; q ist die Normalkoordinate der Molekülschwingung, die die Verzerrung des Moleküls aus der Ruhelage beschreibt.

ψ ist nun eine Funktion von q.

Wirkt auf ein so verzerrtes Molekül ein elektrisches Feld ein, dann wird die Eigenfunktion zusätzlich gestört und erhält im Anschluß an die früheren Rechnungen die Form:

$$\psi = \psi_0 (1 + \epsilon q)(1 + \lambda z)$$

Damit wird das Dipolmoment

$$\mu = e \int z (1 + \epsilon q)^2 (1 + \lambda z)^2 \psi_0{}^* \psi_0 d\tau$$

Legt man den Koordinatenursprung wie immer so, daß $\bar{z}$ verschwindet, und vernachlässigt man die Glieder mit λ^2, dann wird

$$\mu = 2e\lambda\overline{z^2}(1 + \epsilon q)^2 \tag{10}$$

Nimmt man zunächst an, daß λ durch die der Schwingung entsprechende Verzerrung des Moleküls nicht verändert wird, dann kann man λ aus Formel (4) in Formel (10) einsetzen und erhält:

$$\mu = 2e\overline{z^2}(1 + \epsilon q)^2 [-2f\overline{z^2}/ae + 8f^3(\overline{z^2})^4/a^3e^3]$$

$$a = -\mu/f = 2e\overline{z^2}(1 + \epsilon q)^2 (2z^2/ae - 8f^2(\overline{z^2})^4/a^3e^3) =$$

$$= a_0\left(1 - \frac{f^2 a_{0,0}{}^{3/2}}{2a^{1/2} e^2}\right) \tag{11}$$

$$\text{mit } a_0 = \frac{4(\overline{z^2})^2(1 + \epsilon q)^2}{a} \text{ und } a_{0,0} = \frac{4(\overline{z^2})^2}{a} \text{ (vergl. Formel 6)}$$

$a_{0,0}$ bedeutet in dieser Formel den Grenzwert von a für unendlich kleine Feldstärke des ruhenden unverzerrten Moleküls.

Nur a_0 ist eine Funktion von q, dargestellt durch Multiplikation mit dem Faktor $(1 + \epsilon q)^2$; $a_{0,0}$ dagegen ist unabhängig von q.

Der Ausdruck $\partial a/\partial q$ läßt sich nun leicht durch Differenzieren ermitteln:

$$\frac{\partial a}{\partial q} = 4e\overline{z^2}\epsilon(1 + \epsilon q)(2z^2/ae - 8f^2(\overline{z^2})^4/a^3e^3) = \frac{\partial a_0}{\partial q}\left(1 - \frac{f^2 a_{0,0}{}^{3/2}}{2a^{1/2} e^2}\right) \tag{12}$$

Es bleibt nur noch zu untersuchen, ob die sicher bestehende Abhängigkeit des λ von q irgend etwas Wesentliches an dem Resultat ändert.

Da bei der Bestimmung von λ, die zu Formel (4) bzw. (F) führte, keine speziellen Annahmen über die Eigenfunktion der betrachteten Elektronenschale gemacht wurden, bleibt Formel (4) auch erhalten, wenn die Eigenfunktion durch die Schwingung verzerrt wird. Es ändert sich dabei bloß der Mittelwert $\overline{z^2}$. Diese Änderung läßt sich leicht ermitteln. Man geht von Formel (4) aus:

$$\lambda_0 = \frac{-2f\overline{z^2}}{ae} + \frac{8f^3(\overline{z^2})^4}{a^3e^3}.$$

Der Index 0 deutet an, daß sich λ auf das unverzerrte Molekül bezieht.

Um das λ des verzerrten Moleküls zu erhalten, ersetzt man jetzt

$$\overline{z^2} \equiv \int z^2\psi^*\psi d\tau \text{ durch } \overline{z^2} = \int z^2(1+\epsilon q)^2\psi_0{}^*\psi_0\, d\tau$$

Damit wird

$$\lambda = -\frac{2f}{ae}\int z^2(1+\epsilon q)^2\psi_0{}^*\psi_0\, d\tau + \frac{8f^3}{a^3e^3}\left[\int z^2(1+\epsilon q)^2\psi_0{}^*\psi_0\, d\tau\right]^4$$

Vernachlässigt man bei der Mittelwertbildung alle Glieder mit höheren Potenzen von ϵ als ϵ^2, dann erhält man näherungsweise:

$$\lambda = \lambda_0[1+\epsilon q(2+\epsilon q)]$$

Setzt man diesen Wert für λ in (10) ein, dann gewinnt man einen Ausdruck der gleichen Form wie Formel (11):

$$\alpha = 2e\overline{z^2}(1+\epsilon q)^4(2\overline{z^2}/ae - 8f^3(\overline{z^2})^4/a^3e^3) = \alpha_0\left(1 - \frac{f^2\,\alpha_{0,0}{}^{3/2}}{2a^{1/2}e^2}\right) \qquad (13)$$

In Formel (13) hat sich gegenüber (11) nur α_0 geändert, während $\alpha_{0,0}$ gleich geblieben ist.

Aus diesem Grund bleibt Formel (12), die den Verfestigungseffekt von $\partial\alpha/\partial q$ beschreibt, vollkommen erhalten, abgesehen davon, daß $\partial\alpha_0/\partial q$ gegenüber (12) einen anderen Wert annimt.

Mit dieser Feststellung ist die Untersuchung des Verhaltens von $\partial\alpha/\partial q$ in starken Feldern beendet. Das Ergebnis, das in Formel (12) mathematisch formuliert ist, konnte nur nach zahlreichen Näherungen in einfacher Form gewonnen werden. Es erscheint mir daher wichtig, den möglichen Einfluß der verschiedenen Vernachlässigungen klarzustellen.

Wesentlich an allen Ableitungen in dieser Arbeit sind die Ansätze für das Störpotential u and das Störglied v, als Funktionen von z. Dadurch gehen in alle Formeln dieser Arbeit, auch bei beliebig hoher Näherung, als *einzige* Moleküleigenschaft nur die Mittelwerte der Potenzen von z ein. Auch der Verfestigungseffekt ist grundsätzlich unabhängig vom Einzelfall, d.h. von der speziellen Form der Elektroneneigenfunktion und von den mehr oder weniger groben Vernachlässigungen insbesondere auch vom Produktansatz für die Eigenfunktionen. Er hängt nur mit dem Nenner der allgemeinen Störformel (1) zusammen, der bei der Differentiation nach λ die negativen Glieder bewirkt.

Da, wie schon gesagt, nur eine einzige Moleküleigenschaft, nämlich $\overline{z^{n}}$, in die Formeln eingeht, bleibt der Verfestigungseffekt auch bei Differentiation nach q unabhängig von den gemachten Vernachlassigungen immer erhalten.

Im *inhomogenen* Feld der Ionen ist allerdings die Voraussetzung dieser Beweisführung nicht mehr gegeben. u and v hängen nicht nur von z sondern auch vom Abstand r der Elektronen von der Molekülachse ab. Diese Abhängigkeit ist zwar meist vernachlässigbar klein (*loc. cit.* 3), ihre Vernachlässigung bedeutet aber immerhin eine Näherung, deren Einfluß auf die Abnahme von $\partial\alpha/\partial q$ genauer untersucht werden müßte.

Zum Schluß möchte ich die physikalischen Konsequenzen von Formel (12) noch einmal zusammenfassen. Sie besagt, daß der Ausdruck $\partial\alpha/\partial q$, der die Abhängigkeit der Polarisierbarkeit von der Normalkoordinate einer Molekülschwingung beschreibt, eine Funktion der Feldstärke ist. Diese Funktion ist so beschaffen, daß ein Verfestigungsglied mit dem Quadrat der Feldstärke zunimmt, wobei die Polarisierbarkeit selbst abnimmt. Die Abnahme ist umso stärker, je größer die Polarisierbarkeit $\alpha_{0,0}$ des unverzerrten Moleküls bei unendlich kleiner Feldstärke ist und kann bei den großen Feldstärken im Inneren von Ionenkristallen bis zu 50% des Grenzwertes $\lim\limits_{f \to 0} \partial\alpha/\partial q$ betragen.

Wendet man diesen Satz auf das Ramanspektrum von Salzpulvern an, dann bedeutet er, daß nach Ausschaltung aller anderen Einflüsse die Intensität des Ramanspektrums, bei gleichem komplexen Anion, mit wachsendem Ionenpotential des Kations abnimmt. Ein Ergebnis, das im großen und ganzen mit dem experimentellen Befund in Einklang steht.

Ich möchte Herrn Prof. Dr. *K. W. F. Kohlrausch* danken, der mich auf die Möglichkeit aufmerksam machte, die Intensität der Ramanstreuung in Kristallpulvern nach obigem Verfahren zu behandeln.

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A NOTE ON UNIQUENESS SETS FOR ENTIRE FUNCTIONS

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1. A sequence $\{a_n\}_{n=1}^{\infty}$ is called a uniqueness set for entire functions of a given class, if for $f(z)$ of the class, $f(a_n) = 0$, $(n = 1, 2, \ldots)$ implies $f(z) \equiv 0$. Let $n(r)$ denote the number of a_n with $|a_n| \leqslant r$, and let

$$\limsup_{r \to \infty} n(r)/r^{\rho} = \mathrm{L}; \quad \liminf_{k \to \infty} n(r)/r^{\rho} = l. \tag{1.1}$$

R. P. Boas, Jr. has proved two general theorems [1, pp. 22–23] which reduce the problem of fundamental sets of the forms $\mathrm{F}(a_n z)$ and $\mathrm{F}(z + a_n)$ to the problem of uniqueness sets for entire functions, and has also proved the following criteria [1, pp. 23–24] for uniqueness sets.

Theorem A.—*The set $\{a_n\}$ is a uniqueness set for functions of order atmost ρ, type less than τ if of order ρ, if*

$$\tau \leqslant \limsup_{r \to \infty} r^{-\rho} \int_0^r t^{-1} n(t)\, dt$$

in particular if

$$\tau \leqslant l/\rho \tag{1.2}$$

or if

$$\tau \leqslant \mathrm{L}/e\rho. \tag{1.3}$$

Theorem B.—*The set $\{a_n\}$ is a uniqueness set for functions of order atmost ρ and of type less than τ if of order ρ, if the a_n are contained in an angle of opening 2α, and either*

$$\limsup_{r \to \infty} r^{1 - \frac{\alpha\rho}{b}} \int_0^{r^{\alpha/b}} n(t)\left(t^{-1-\frac{b}{\alpha}} + t^{-1+\frac{b}{\alpha}} r^{-2}\right) dt$$

$$\geqslant \frac{2\alpha\,\tau}{\pi \mathrm{B}} \frac{\alpha^2\rho^2}{\alpha^2\rho^2 - b^2}; \quad (\alpha > b/\rho)$$

or

$$\limsup_{r \to \infty} \frac{1}{\log r} \int_0^{r^{1/b}} n(t)\,(t^{-1-\rho} + t^{-1+\rho}\, r^{\;2}\, dt) \geqslant \{\tau \sec \alpha\rho\}/\rho\pi; \quad (\alpha \leqslant b/\rho)$$

in particular if

$$\tau \leqslant (\pi \mathrm{B}l)/\alpha\rho \qquad (\alpha > b/\rho) \tag{1·5}$$

or

$$\tau \leqslant \pi l \cos(\alpha\rho) \qquad (\alpha \leqslant b/\rho) \tag{1·6}$$

here $\mathrm{B} = b \cos b$ *is the maximum of* $x \cos x$ *in* $(0, \pi/2)$.

In this note I give criteria for uniqueness sets more general than (1·2), (1·3) and (1·5). Let

$$\limsup_{r \to \infty} \log \mathrm{M}(r)/r^{\rho} = \mathrm{T}; \ \liminf_{r \to \infty} \log \mathrm{M}(r)/r^{\rho} = t.$$

THEOREM 1.—*The set* $\{a_n\}$ *is a uniqueness set for functions of order atmost* $\rho\,(0 < \rho < \infty)$, *and lower type* $\leqslant t$ *and type* $\leqslant \mathrm{T}$ *if of order* ρ, *if either*

$$t < l/\rho \tag{1.7}$$

or

$$\mathrm{T} < (e\rho)^{-1}\ \mathrm{L} \exp(l/\mathrm{L}) \tag{1·8}$$

in particular if

$$\mathrm{T} < (2e\,\rho)^{-1}\,[\mathrm{L} + l + \surd(\mathrm{L}^2 + 3l^2 + 2l\mathrm{L}] \tag{1·9}$$

or if

$$\mathrm{T} < (e\,\rho)^{-1}\,(\mathrm{L} + l) \tag{1·10}$$

or if

$$\mathrm{T} \leqslant l/\rho;\ \textit{and}\ l < \mathrm{L}. \tag{1·11}$$

THEOREM 2.—*The set* $\{a_n\}$ *is a uniqueness set for functions of order atmost* ρ, *and of type less than or equal to* T *if of order* ρ, *if the* a_n *are contained in an angle of opening* 2α, $b/\rho < \alpha < \pi$, *and if*

$$\mathrm{T} < \frac{\pi \mathrm{BL}}{\alpha\rho}\left\{1 + \frac{b\,(\mathrm{L} - l)}{\rho\alpha\mathrm{L}}\right\}^{-\frac{1}{2}\left(\frac{\alpha\rho}{b} - 1\right)}\left\{1 - \frac{b\,(\mathrm{L} - l)}{\rho\alpha\mathrm{L}}\right\}^{\frac{1}{2}\left(\frac{\alpha\rho}{b} + 1\right)} \tag{1.12}$$

Here B and b have the same meanings as in Theorem B.

We note that condition (1·7) implies $l > 0$ and any one of the conditions (1.8) to (1·12) implies that $\mathrm{L} > 0$. In §5 and §6 we construct functions to show that (1.7) and (1.8) are best possible conditions.

2. Theorem 1 is equivalent to the following lemma.

LEMMA 2.1.—*If* $f(z)$ *is an entire function of order* ρ *and type* T *and lower type* t, *and if* $n(r)$ *denotes the number of zeros of* $f(z)$ *in* $|z| \leqslant r$ *and* L *and* l *have the same meanings as in* (1.1) *then*

$$l \leqslant \rho t \tag{2.2}$$

$$le \leqslant \mathrm{L} \exp(l/\mathrm{L}) \leqslant \rho \mathrm{T} e \tag{2.3}$$

$$\mathrm{L} + l + \surd(\mathrm{L}^2 + 3l^2 + 2l\mathrm{L}) \leqslant 2\rho \mathrm{T} e \tag{2.4}$$

$$\mathrm{L} + l \leqslant \rho \mathrm{T} e \tag{2.5}$$

$$l < \rho \mathrm{T} \text{ if } l < \mathrm{L} \tag{2.6}$$

Proof.—By Jensen's Theorem, if $a \geqslant 1$

$$\int_0^{ra^{1/\rho}} \frac{n(x)}{x}\,dx < k + \log \mathrm{M}\,(ra^{1/\rho})$$

Hence[1]

$$(l-\epsilon)\frac{r^\rho}{\rho} + n(r)\int_r^{ra^{1/\rho}} \frac{dx}{x} < k + \log \mathrm{M}\,(ra^{1/\rho}) \tag{2·7}$$

and so [2, p. 82]

$$(l + \mathrm{L}\log a)/(\rho a) \leqslant \mathrm{T}.$$

The left-hand side is maximum when $a = \exp[(\mathrm{L} - l)/\mathrm{L}]$. Hence

$$\mathrm{T} \geqslant \frac{\mathrm{L}}{\rho e}\,e^{l/\mathrm{L}} \geqslant \frac{\mathrm{L}}{\rho e}\left\{1 + \frac{l}{\mathrm{L}} + \frac{l^2}{2\mathrm{L}^2}\right\}$$

Hence

$$\mathrm{T} \geqslant \mathrm{L}/(\rho e) \text{ and } \rho\, e\mathrm{T} \geqslant \mathrm{L} + l + l^2/(2\rho\, e\mathrm{T})$$

which gives

$$2\rho e\mathrm{T} \geqslant \mathrm{L} + l + \sqrt{(\mathrm{L}^2 + 3l^2 + 2l\mathrm{L})} \geqslant 2\,(\mathrm{L} + l).$$

Further taking $a = 1$ in (2.7) we get

$$l \leqslant \rho t.$$

Now e^x/x has only one minimum point, $x = 1$. Hence $e^x \geqslant ex$ equality if $x = 1$. Hence

$$e^{l/\mathrm{L}} \geqslant (el)/\mathrm{L} \text{ equality if } l = \mathrm{L}$$

and so

$$\mathrm{T} \geqslant \frac{\mathrm{L}}{\rho e}\,e^{l/\mathrm{L}} \geqslant \frac{l}{\rho}$$

and $\mathrm{T} > l/\rho$ if $l < \mathrm{L}$.

3. Theorem 2 is equivalent to the following lemma.

LEMMA 3·1.—*If $f(z)$ is of order ρ and type T, if $f(z)$ has zeros $a_n = r_n\,e^{i\theta_n}$ with $|\,\theta_n\,| \leqslant \alpha < \pi$, and if $n(r)$ denotes the number of a_n with $|\,a_n\,| \leqslant r$, then*[2]

$$\mathrm{T} \geqslant \frac{\pi \mathrm{BL}}{\alpha\rho}\left\{1 + \frac{b(\mathrm{L} - l)}{\rho\alpha\mathrm{L}}\right\}^{-\frac{1}{2}\left(\frac{\alpha\rho}{b}-1\right)}\left\{1 - \frac{b(\mathrm{L} - l)}{\rho\alpha\mathrm{L}}\right\}^{\frac{1}{2}\left(\frac{\alpha\rho}{b}+1\right)} \tag{3.2}$$

$$\geqslant \frac{\pi \mathrm{B}l}{\alpha\rho}$$

$$\mathrm{T} > (\pi \mathrm{B}1)/(\alpha\rho) \textit{ if } l < \mathrm{L}. \tag{3.3}$$

Here *$\alpha > b/\rho$ **and** L, l, B and b have the same meanings as before.*

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[1] k denotes a constant not necessarily the same at each occurrence.

[2] We suppose in this lemma that $\mathrm{L} > 0$. If $\mathrm{L} = 0$ we have from (3·4) an obvious result $\mathrm{T} \geqslant 0$.

Proof.—Let the integral in (1.4) be denoted by $I = I(r)$. Boas has proved [1, pp. 28–29] that if $a > b/\rho$

$$\limsup_{R\to\infty} R^{1-\frac{a\rho}{b}} I(R) \leqslant \frac{2aT}{\pi B}\,\frac{a^2\rho^2}{a^2\rho^2 - b^2}$$

Let $0 < c < 1$. Then

$$I(R) > (l-\epsilon)\int_{r_0}^{cR^{a/b}} \{t^{\rho-1-\frac{b}{a}} + t^{\rho-1+\frac{b}{a}} R^{-2}\}\, dt$$

$$+\, n(cR^{a/b}) \int_{cR^{a/b}}^{R^{a/b}} (t^{-1-\frac{b}{a}} + t^{-1+\frac{b}{a}} R^{-2})\, dt.$$

Hence

$$\frac{2aT}{\pi B}\,\frac{a^2\rho^2}{a^2\rho^2 - b^2} \geqslant \limsup_{R\to\infty} R^{1-\frac{a\rho}{b}} I(R)$$

$$\geqslant l\left\{\frac{c^{\rho-\frac{b}{a}}}{\rho-\frac{b}{a}} + \frac{c^{\rho+\frac{b}{a}}}{\rho+\frac{b}{a}}\right\} + \frac{La}{b}\,(c^{-b/a} - c^{b/a})\, c^{\rho}. \tag{3.4}$$

The right-hand side is maximum when

$$c = \left\{\frac{L\rho a - b(L-l)}{L\rho a + b(L-l)}\right\}^{a/2b}$$

Hence we have

$$T \geqslant \frac{\pi B(a^2\rho^2 - b^2)}{2a^2\rho^2}\left\{\frac{L\rho a - b(L-l)}{L\rho a + b(L-l)}\right\}^{\frac{\rho a}{2b}} \frac{\sqrt{(L^2\rho^2a^2 - b^2(L-l)^2)}}{b} \times$$

$$\left\{\frac{1}{\rho a - b} - \frac{1}{\rho a + b}\right\}$$

which proves the left-hand side of (3·2). Let the middle expression in (3.2) be denoted by M. Then

$$M \leqslant (\pi BL)/(a\rho)$$

Consider now

$$y = (1-x)^{1+\theta}(1+x)^{-\theta} - \{1 - (1+2\theta)x\} \text{ where } \theta > 0,\ 0 \leqslant x \leqslant 1$$

$$\frac{dy}{dx} = (1+\theta)\left\{1 - \left(\frac{1-x}{1+x}\right)^{\theta}\right\} + \theta\left\{1 - \left(\frac{1-x}{1+x}\right)^{\theta+1}\right\} \geqslant 0$$

for all $x \leqslant 1$, equality if $x = 0$. Further $y(0) = 0$. Hence $y(x) \geqslant 0$ if $0 \leqslant x \leqslant 1$, equality if $x = 0$. Writing

$$x = \frac{b(L-l)}{\rho\, aL} \leqslant \frac{b}{\rho a} < 1;\ \theta = \tfrac{1}{2}\left(\frac{a\rho}{b} - 1\right) > 0$$

we obtain

$$M \geqslant \frac{\pi BL}{a\rho} \frac{l}{L} = \frac{\pi Bl}{a\rho}$$

equality if $L = l$ only. Hence the lemma is proved.

4. The condition (1.12) requires $\rho > b/a$ and gives a better result than (1·8) when $(L - l)/L$ is a small number and $b/\rho < a < \pi B$. If $\rho \leqslant b/a$ the corresponding condition is (1·6) which is weaker than (1.8) if $\rho \cos a\rho \leqslant 1/\pi$. This range of values of ρ, for which (1.8) will be stronger than (1·6), increases as l/L diminishes. For instance, if $l/L = 1/100$ then so long as $\rho \cos a\rho \leqslant 37/\pi$ the condition (1.8) will give a larger upper bound for T than (1.6).

5. To show that (2.2) is best possible, we construct an entire function $f(z)$ for which $l = \rho t$. For the function given by Boas [1, pp. 31–32], $\rho t - l$ is not zero but can be made arbitrarily small.

THEOREM 3:—*For each positive ρ and each positive t, there exists an entire function $f(z)$ of order ρ, type t, with zeros a_n such that*

$$l = \liminf_{n \to \infty} n\, |a_n|^{-\rho} = \rho t. \tag{5·1}$$

Let

$$a_n = n^{2/\rho}/(2\rho t)^{1/\rho}$$

$$f(z) = \prod_{\nu=1}^{\infty} \left(1 + \frac{z^\nu}{a_\nu{}^\nu}\right) \tag{5·2}$$

We have then

$$n\,(a_n) = 1 + 2 + \ldots . + n = \frac{n^2}{2} + O\,(n) \sim \rho t a_n{}^\rho$$

If $a_n \leqslant r < a_{n+1}$

$$n\,(r) = n\,(a_n) \sim \rho t a_n{}^\rho \sim \rho t r^\rho. \quad \text{Hence } l = \rho t.$$

Now let $r = a_n$

$$\begin{aligned} \log f\,(r) &= \sum_{\nu=1}^{n-1} \log\left(1 + \frac{r^\nu}{a_\nu{}^\nu}\right) + \log 2 + \sum_{n+1}^{\infty} \log\left(1 + \frac{r^\nu}{a_\nu{}^\nu}\right) \\ &= \Sigma_1 \qquad\qquad\qquad\qquad + \log 2 + \Sigma_2 \,(\text{say}). \end{aligned}$$

Now

$$\begin{aligned} \Sigma_2 &= \sum_{k=1}^{\infty} \log\left\{1 + \left(\frac{n}{n+k}\right)^{2(n+k)/\rho}\right\} \\ &= \sum_{k=1}^{n} + \sum_{n+1}^{\infty} = O\,(n) \end{aligned}$$

and

$$\Sigma_1 = \log \frac{a_1 + a_n}{a_1} \frac{a_2{}^2 + a_n{}^2}{a_2{}^2} \cdots . \frac{a_{n-1}{}^{n-1} + a_n{}^{n-1}}{a_{n-1}{}^{n-1}}$$

Since

$$\nu \log (a_n/a_\nu) < \log \frac{a_n^\nu + a_\nu^\nu}{a_\nu^\nu} < \log 2 + \nu \log \frac{a_n}{a_\nu}$$

Hence

$$\begin{aligned}\Sigma_1 &= \mathrm{O}(n) + \log \frac{a_n^{1+2+\dots(n-1)}}{a_1\, a_2^2 \dots a_{n-1}^{(n-1)}} \\ &= \frac{n^2}{2} \log a_n + \mathrm{O}(n \log n) - \left[\sum_1^{n-1}\left(\frac{2}{\rho} k \log k - \frac{k}{\rho} \log (2\rho t)\right)\right] \\ &= \frac{n^2}{2\rho} + o(n^2)\end{aligned}$$

changing n to $(n+1)$

$$\log f(a_{n+1}) = \frac{n^2}{2\rho} + o(n^2)$$

Hence if $a_n \leqslant r < a_{n+1}$ we have

$$\log f(a_n) \leqslant \log f(r) < \log f(a_{n+1})$$

and so

$$\log \mathrm{M}(r) = \frac{n^2}{2\rho} + o(n^2) \sim tr^\rho.$$

6. When $l = 0$ we have from (2·3) that $\mathrm{L} \leqslant \rho \mathrm{T} e$. In this section we construct a function $f(z)$ to show that this relation is best possible. A similar function, for the same purpose, has been constructed by Boas [1, pp. 30–31]. We consider also, a particular sequence $\mathrm{R}(n) = \mathrm{R}$ such that $\log \mathrm{M}(\mathrm{R}, f) \sim \mathrm{TR}^\rho$, and prove that $n(\mathrm{S}) \sim \mathrm{LS}^\rho$ where $\mathrm{S} = \mathrm{S}(n) = \mathrm{R}(n) e^{-1/\rho}$ and $\mathrm{L} = \rho e \mathrm{T}$.

THEOREM 4.—*For each positive* ρ, *and each positive* T, *there exists an entire function* $f(z)$ *of order* ρ *and type* T, *with zeros* a_n *such that*

$$\mathrm{T} = \limsup_{r \to \infty} \log \mathrm{M}(r)/r^\rho = \lim_{n \to \infty} \log \mathrm{M}\{\mathrm{R}(n)\}/\{\mathrm{R}(n)\}^\rho \tag{6·1}$$

$$\mathrm{L} = \limsup_{r \to \infty} n(r)/r^\rho = \lim_{n \to \infty} n\{\mathrm{S}(n)\}/\{\mathrm{S}(n)\}^\rho = \rho e \mathrm{T} \tag{6·2}$$

$$t = \liminf_{r \to \infty} \log \mathrm{M}(r)/r^\rho = \lim_{n \to \infty} \log \mathrm{M}\{\mathrm{S}(n)\}/\{\mathrm{S}(n)\}^\rho = 0 \tag{6·3}$$

where $\{\mathrm{R}(n)\} \uparrow \infty$ and $\mathrm{S}(n) = \mathrm{R}(n) e^{-1/\rho}$

Let $\mathrm{F}(n) = 2^{\mathrm{F}(n-1)}$; $\mathrm{F}(1) = 2$ $(n = 2, 3, \dots)$

$\mathrm{S}(n) = \{\mathrm{F}(n)/\rho e \mathrm{T}\}^{1/\rho}$; $\mathrm{R}(n) = \mathrm{S}(n) e^{1/\rho}$; $(n = 1, 2, 3, \dots)$

$$f(z) = \prod_1^\infty \left\{1 + \left(\frac{z}{\mathrm{S}(n)}\right)^{\mathrm{F}(n)}\right\}$$

$f(z)$ is an entire function.

$$f(\mathrm{R}(n)) = \mathrm{M}(\mathrm{R}(n)) = \Pi_1 \Pi_2 \Pi_3$$

where

$$\Pi_1 = \prod_{\nu=1}^{n-1} \left\{1 + \left(\frac{\mathrm{R}(n)}{\mathrm{S}(\nu)}\right)^{\mathrm{F}(\nu)}\right\}$$

Hence

$$\frac{\log \Pi_1}{\{\mathrm{R}(n)\}^{\rho}} \leqslant \Big\{ \{\log 2\big(\mathrm{R}(n)\big)^{\mathrm{F}(n-1)} - \mathrm{F}(n-1)\log\big(\mathrm{S}(n-1)\big)$$

$$+ (n-2)\,\mathrm{F}(n-2)\log\ \{2\,\mathrm{R}(n)\}\Big\}\ \{\mathrm{R}(n)\}^{\rho}$$

$$\to 0 \text{ as } n \to \infty$$

$$\Pi_2 = \left\{1 + \left(\frac{\mathrm{R}(n)}{\mathrm{S}(n)}\right)^{\mathrm{F}(n)}\right\} = l + e^{\mathrm{F}(n)/\rho}$$

$$\frac{\log \Pi_2}{\{\mathrm{R}(n)\}^{\rho}} \sim \frac{\mathrm{F}(n)}{\rho}\,\frac{\rho \mathrm{T}}{\mathrm{F}(n)} = \mathrm{T}$$

Further

$$\Pi_3 = \prod_{\nu=n+1}^{\infty} \left\{1 + \left(\frac{\mathrm{R}(n)}{\mathrm{S}(\nu)}\right)^{\mathrm{F}(\nu)}\right\}$$

and

$$\left\{\frac{\mathrm{R}(n)}{\mathrm{S}(n+k)}\right\}^{\mathrm{F}(n+k)} < (\tfrac{1}{2})^{\mathrm{F}(n+k)} \text{ if } k \geqslant 1;\ n \geqslant n_0$$

Hence

$$\Pi_3 < e^{\sum\limits_{1}^{\infty} (\frac{1}{2})^{\mathrm{F}(n+k)}} < e$$

and therefore

$$\lim_{n \to \infty} \frac{\log \mathrm{M}\{\mathrm{R}(n)\}}{\{\mathrm{R}(n)\}^{\rho}} = \mathrm{T}$$

Let now $\mathrm{S}(n) \leqslant r < \mathrm{S}(n+1)$. Then

$$f(r) = \prod_{1}^{n-1} \cdot \left[1 + \left(\frac{r}{\mathrm{S}(n)}\right)^{\mathrm{F}(n)}\right]\left[1 + \left(\frac{r}{\mathrm{S}(n+1)}\right)^{\mathrm{F}(n+1)}\right] \times$$

$$\prod_{n+2}^{\infty} = \Pi_1 \Pi_2 \Pi_3 \Pi_4 \text{ (say)}$$

Then

$$\log \Pi_1 = o\,(r^{\rho}).$$

If $r = \mathrm{S}(n)$, $\Pi_2 = 1$. If $r > \mathrm{S}(n)$ then for all large n

$$\frac{\log \Pi_2}{r^{\rho}} \sim \frac{\mathrm{F}(n)\log r/\mathrm{S}(n)}{r^{\rho}} = \frac{\mathrm{F}(n)}{\{\mathrm{S}(n)\}^{\rho}}\,\frac{\log\{r/\mathrm{S}(n)\}}{\{r/\mathrm{S}(n)\}^{\rho}}$$

$$\leqslant \frac{\rho e \mathrm{T}}{\rho e} = \mathrm{T}$$

since $\dfrac{\log x}{x^{\rho}} \leqslant \dfrac{1}{\rho e}$ for all $x \geqslant 1$.

Further $\Pi_3 \leqslant 2$; $\Pi_4 < e$

Hence

$$\limsup_{r\to\infty} \frac{\log M(r)}{r^{\rho}} = T.$$

If $r = S(n)$, we have

$$t = \liminf_{r\to\infty} \frac{\log M(r)}{r^{\rho}} = \lim_{n\to\infty} \frac{\log M\{S(n)\}}{\{S(n)\}^{\rho}} = 0$$

Further

$$n\{S(n)\} = F(1) + \ldots . + F(n) \sim F(n)$$

$$\frac{n\{S(n)\}}{\{S(n)\}^{\rho}} \sim \rho e T.$$

Since $L \leqslant \rho e T$ we have

$$L = \limsup_{r\to\infty} \frac{n(r)}{r^{\rho}} = \lim_{n\to\infty} \frac{n\{S(n)\}}{\{S(n)\}^{\rho}} = \rho e T.$$

Also

$$l = \liminf_{r\to\infty} \frac{n(r)}{r^{\rho}} = \lim_{n\to\infty} \frac{n(S(n) - 1)}{\{S(n) - 1\}^{\rho}} = 0$$

If $n > n_0$, $n\{R(n)\} = n\{S(n)\}$

and hence $\lim\limits_{n\to\infty} n\{R(n)\}/\{R(n)\}^{\rho} = \rho T.$

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ON THE HARMONIC SUMMABILITY OF FOURIER SERIES

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1. Let $f(x)$ be a function integrable in the sense of Lebesgue and periodic with period 2π. Let the Fourier Series associated with $f(x)$ be

$$\tfrac{1}{2}a_0 + \sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx). \tag{1·1}$$

A sequence $\{s_n\}$ is said to be summable by *harmonic means*, if

$$\lim_{n\to\infty} \frac{1}{\log n} \sum_{k=0}^{n} \frac{s_{n-k}}{k+1} \tag{1·2}$$

exists. This method of summability which belongs to the class of generalized regular Nörlund methods*, was introduced for the first time by M. Riesz† who proved that every series summable by harmonic means is summable (C, δ), $\delta > 0$.

The application of harmonic summation to Fourier Series has been discussed by Juringius‡, Hille and Tamarkin§ and Iyengar§§. In this paper I prove the following theorem:—

Theorem.—*The Fourier Series of the function $f(x)$ is summable by harmonic means at a point x at which*

$$g_1(t) = \int_0^t |g(u)|\,du = 0\left(\frac{t}{\log \frac{1}{t}}\right). \tag{1·3}$$

where

$$g(t) = f(x+t) + f(x-t) - 2f(x).$$

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* Nörlund (8).

† Riesz (9).

‡ A proof of the theorem that the Fourier Series is not summable by harmonic means almost everywhere had been worked out by him but remains unpublished. See Hille and Tamarkin (4), (5).

§ Hille and Tamarkin (4), (5).

§§ Iyengar (6), (7).

2. In order to prove the theorem we shall require the following lemmas:

Lemma I*. *If* $0 < t < \pi$, *then*

$$\left| \sum_{k=0}^{n} \frac{\cos (k+1) t}{k+1} \right| < A \left(1 + \log \frac{1}{t}\right).$$

Lemma II†. *For all values of n and x*

$$\left| \sum_{k=0}^{n} \frac{\sin (k+1) t}{k+1} \right| \leqslant \tfrac{1}{2}\pi + 1.$$

3. *Proof of the Theorem.* Let $s_n(x)$ denote the n-th partial sum of the series (1·1). It is well-known that

$$s_n(x) - f(x) = \frac{1}{2\pi} \int_0^{\pi} g(t) \frac{\sin (n+\frac{1}{2}) t}{\sin \frac{1}{2} t}\, dt. \tag{3·1}$$

Making use of the formula (1·2), we obtain

$$\begin{aligned} &\frac{1}{\log n} \sum_{k=0}^{n} \frac{1}{k+1} \{s_{n-k} - f(x)\} \\ &= \frac{1}{\log n} \sum_{k=0}^{n} \frac{1}{k+1} \cdot \frac{1}{2\pi} \int_0^{\pi} g(t) \cdot \frac{\sin (n-k+\frac{1}{2}) t}{\sin \frac{1}{2} t}\, dt \\ &= \int_0^{\pi} g(t) \cdot \frac{1}{2\pi \log n} \sum_{k=0}^{n} \frac{1}{k+1} \frac{\sin (n-k+\frac{1}{2}) t}{\sin \frac{1}{2} t}\, dt \\ &= \int_0^{\pi} g(t)\, N_n(t)\, dt. \end{aligned}$$

In order to prove the theorem we have to show that

$$\int_0^{\pi} g(t)\, N_n(t)\, dt = o(1), \tag{3·2}$$

as $n \to \infty$, when (1·3) holds.

We set

$$\begin{aligned} \int_0^{\pi} g(t)\, N_n(t)\, dt &= \left(\int_0^{\frac{1}{n}} + \int_{\frac{1}{n}}^{\delta} + \int_{\delta}^{\pi}\right) g(t)\, N_n(t)\, dt \\ &= L_1 + L_2 + L_3. \end{aligned}$$

Now

$$\begin{aligned} L_1 &= \int_0^{\frac{1}{n}} g(t)\, N_n(t)\, dt \\ &= O\left(\int_0^{\frac{1}{n}} |g(t)| \cdot n\, dt\right) \end{aligned}$$

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* For proof refer to Hardy and Rogosinski (3).

† Gronwall (1), Titchmarsh (10), p. 440.

$$= O\left(g_1\left(\frac{1}{n}\right) \cdot n\right)$$

$$= O\left(\frac{1}{\log n}\right) = O(1), \tag{3·3}$$

since $N_n(t) = O(n)$‡ for all t such that $0 \leqslant t \leqslant \pi$.

Also by virtue of Riemann-Lebesgue theorem and the regularity of the method of summation, we have

$$L_3 = \int_\delta^\pi g(t)\, N_n(t)\, dt$$

$$= O(1). \tag{3·4}$$

Lastly, in order to show that $L_2 = O(1)$ we require a suitable estimate for the kernel $N_n(t)$ in the interval $\left(\frac{1}{n}, \delta\right)$. Since

$$N_n(t) = \frac{1}{2\pi \log \frac{1}{t} \cdot \sin \frac{1}{2} t} \times$$

$$\left\{\sin\left(n + \frac{3}{2}\right) t \sum_{k=0}^{n} \frac{\cos(k+1)t}{k+1} - \cos\left(n + \frac{3}{2}\right) t \sum_{k=0}^{n} \frac{\sin(k+1)t}{k+1}\right\},$$

by making use of Lemmas I and II, we get

$$N_n(t) = O\left[\frac{1}{t \log n}\left\{1 + \log \frac{1}{t}\right\}\right].$$

Hence

$$L_2 = \int_{\frac{1}{n}}^{\delta} g(t)\, N_n(t)\, dt = O\left(\int_{\frac{1}{n}}^{\delta} |g(t)| \cdot |N_n(t)|\, dt\right)$$

$$= O\left(\frac{1}{\log n} \int_{\frac{1}{n}}^{\delta} |g(t)| \frac{dt}{t}\right)$$

$$+ O\left(\frac{1}{\log n} \int_{\frac{1}{n}}^{\delta} |g(t)| \cdot \frac{1}{t} \log \frac{1}{t}\, dt\right)$$

$$= O\left(\frac{1}{\log n} \cdot g_1(t) \cdot \frac{1}{t}\Big]_{\frac{1}{n}}^{\delta} + \frac{1}{\log n} \int_{\frac{1}{n}}^{\delta} g_1(t) \frac{dt}{t^2}\right)$$

$$+ O\left(\frac{1}{\log n} \cdot g_1(t) \cdot \log \frac{1}{t} \cdot \frac{1}{t}\Big]_{\frac{1}{n}}^{\delta}\right.$$

$$\left. + \frac{1}{\log n} \int^{\delta} g_1(t) \cdot \left\{1 + \log \frac{1}{t}\right\} \frac{dt}{t^2}\right)$$

---

‡ This result can be established with the help of the inequality $|\sin nt| \leqslant n |\sin t|$ and the relation $\sum^{n} \frac{1}{k+1} \simeq \log n$. See also Hille and Tamarkin (5).

$$= O\left(\frac{1}{\log n}\right) + O\left(\frac{1}{(\log n)^2}\right) + 0\left(\frac{1}{\log n}\right)$$

$$+ 0\left(\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} \frac{dt}{t \log \frac{1}{t}}\right) + 0\left(\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} \frac{dt}{t}\right)$$

$$= 0(1) + 0\left(\frac{\log \log \frac{1}{t}}{\log n}\Big]_{1}^{\delta}\right) + 0\left(\frac{\log \frac{1}{t}}{\log n}\Big]_{\frac{1}{n}}^{\delta}\right) = 0(1). \tag{3.5}$$

Combining (3·3), (3·4) and (3·5) we see that (3·2) holds. This proves the theorem.

4. Iyengar* has proved the undernoted theorem:—

If the series $\sum_{0}^{\infty} a_n$ *is summable by harmonic means and* $a_n > -An^{-\delta}$, $0 < \delta < 1$, *then the series is convergent.* It may be remarked that the theorem of this paper taken in conjunction with the above mentioned theorem of Iyengar gives another proof of the following well-known theorem of Hardy and Littlewood†:—

If (i) $a_n, b_n > -An^{-\delta}$ *and (ii)* $\int_0^t |g(u)|\, du = 0\left(\frac{t}{\log \frac{1}{t}}\right)$, *then the Fourier Series converges to* $f(x)$.

5. Iyengar‡ has proved a theorem, *viz.*,

If $g(t) = 0\left(\frac{1}{\log \frac{1}{t}}\right)$, *then the Fourier Series of* $f(x)$ *is summable by harmonic means to* $f(x)$.

This theorem of Iyengar and the theorem of this paper can both be proved indirectly by making use of a result of Hille and Tamarkin. Hille and Tamarkin§ have established the following results:—

THEOREM.—*A necessary and sufficient condition that the n-th harmonic mean of a Fourier Series shall converge to* $f(x)$ *at a point* x *at which* $\int_0^t |g(u)|\, du = 0(t)$, *is that*

$$\lim_{n \to \infty} \frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} \sin nt \cdot \log \frac{1}{t} \cdot g(t) \cdot \frac{dt}{t} = 0. \tag{5·1}$$

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* Iyengar (6), Theorem I.

† Hardy and Littlewood (2).

‡ Iyengar (6), Theorem II.

§ Hille and Tamarkin (5).

If we assume Iyengar's condition, *viz.*,

$$g(t) = o\left(\frac{1}{\log \frac{1}{t}}\right).$$

then the integral (5·1), *viz.*

$$\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} \sin nt \cdot \log \frac{1}{t} \cdot g(t)\,\frac{dt}{t} = O\left(\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} |\,g(t)\,| \cdot \log \frac{1}{t} \cdot \frac{dt}{t}\right)$$

$$= 0\left(\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} \frac{dt}{t}\right)$$

$$= 0(1).$$

On the other hand if we assume the condition of the theorem of this paper, *viz.*,

$$g_1(t) = \int_0^t |\,g(u)\,|\,du = 0\left(\frac{t}{\log \frac{1}{t}}\right),$$

then working on the lines of the last paragraph of § 3, it can be shown that under this condition the integral (5·1) is 0(1). In view of the great complication and difficulty involved in establishing (5·1), the proof of the theorem as given here may be preferable.

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ON A BESSEL FUNCTION OF THE SECOND KIND AND WILKS' Z-DISTRIBUTION

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Wilks[1] studied the distribution of $Z = B\theta_1\theta_2 \ldots \theta_n$, where θ_i has the distribution

$$dF = \frac{1}{\Gamma(a_i)} \theta_i^{a_i - 1} e^{-\theta_i} d\theta_i; \qquad (i = 1, 2, \ldots n)$$

He succeeded in integrating the distribution of Z for $n = 2$ and $a_1 = \frac{1}{2}(N-1)$ and $a_2 = \frac{1}{2}(N-2)$. Later Chung Tsi Hsu[2] derived the distribution of Z for $n = 2$ and for any values a_1 and a_2 in connection with certain tests of hypotheses for samples from two Bivariate Normal populations. The distribution is derived in the form

$$dF = \frac{2\sqrt{\pi}\, Z^{a_2-1}\, e^{-2\sqrt{(Z/B)}}\, dZ}{B^{a_2}\, \Gamma(a_1)\, \Gamma(a_2)\, \Gamma(a_1 - a_2 + \frac{1}{2})} \times$$

$$\int_0^\infty e^{-2x} 2\sqrt{(Z/B)} + x^{a_1 - a_2 - \frac{1}{2}}\, x^{a_1 - a_2 - \frac{1}{2}}\, dx \tag{1}$$

Taking $B = 1$, $a_1 = a_2 = \frac{1}{2}(N-1)$, this becomes

$$dF = \frac{2\sqrt{\pi}\, Z^{a_2-1}\, e^{-2\sqrt{Z}}}{\Gamma^2(a_2)} dZ \int_0^\infty e^{-2x} (2\sqrt{Z} + x)^{-\frac{1}{2}}\, x^{-\frac{1}{2}}\, dx \tag{2}$$

He says " Since (2) can apparently not be simplified, I have been unable thus far to find in manageable form the distribution of the ratio $\frac{Z_1}{Z_2}$ and therefore of $\frac{u''}{u'}$. So he used the alternative criterion $\omega = Z - Z'$ (or $Z_1 - Z_2$) for the hypothesis H_1 that he considered.

2. In this paper I have derived the distribution of $\frac{Z_1}{Z_2}$ in the most general case by the use of Bessel Function of the second kind and the particular case follows immediately.

Now (1) can be written, changing the variable to $t = 2\sqrt{(Z/B)}$, and $2x = \xi$, as

$$dF = \frac{1}{2^{a_1+a_2-2}\,\Gamma(a_1)\,\Gamma(a_2)}\, t^{a_1+a_2-1} k_{a_1-a_2}(t)\, dt \tag{3}$$

where $k_\lambda(t)$ is a Bessel Function of the second kind.

Thus we have to consider a distribution of the form

$$dF = y_4\, y_0\, x^m\, k_n(x)\, dx \qquad (x > a) \tag{4}$$

The distribution given by

$$dF = y_0\, e^{-cx/b}\, |x|^m \left\{ \begin{matrix} \pi\, I_m(x/b) \\ \text{or} \\ k_m(x/b) \end{matrix} \right\} dx \tag{5}$$

and

$$dF = y_0 x^m\, k_m(x)\, dx \tag{6}$$

have been studied by A. T. McKay[3] and Karl Pearson[4,5] respectively. So far I am not aware of the distribution(4) being studied.

3. *Moments of the Distribution* (4).—The constant y_0 is given by

$$1 = y_0 \int_0^\infty x^m\, k_n(x)\, dx$$

$$= y_0\, 2^{m-1}\, \Gamma\left(\frac{m+1+n}{2}\right) \Gamma\left(\frac{m+1-n}{2}\right) \ldots\ [cf.^6]$$

i.e.,

$$y_0 = 1/2^{m-1}\, \Gamma\left(\frac{m+1+n}{2}\right) \Gamma\left(\frac{m+1-n}{2}\right) \tag{7}$$

The moment generating function is

$$M(t) = y_0 \int_0^\infty e^{tx}\, x^m\, k_n(x)\, dx$$

$$= y_0 \sqrt{\frac{\pi}{2}}\, \frac{\Gamma(m-n+1)\, \Gamma(m+n+1)}{\Gamma(m+\frac{3}{2})\,(1-t^2)^{m+\frac{1}{2}}} \times$$

$$F\left(-n+\tfrac{1}{2},\ n+\tfrac{1}{2},\ m+\tfrac{3}{2},\ \tfrac{1}{2}(1+t)\right).$$

or

$$= y_0 \int_0^\infty \left\{ \sum_{r=0}^{\infty} \frac{t^r}{r!}\, x^{m+r}\, k_n(x) \right\} dx.$$

Integrating term by term we get

$$M(t) = y_0 \sum_{r=0}^{\infty} \frac{t^r}{r!} \int_0^\infty x^{m+r}\, k_n(x)\, dx$$

$$= y_0 \sum_{r=0}^{\infty} \frac{t^r}{r!}\, 2^{m+r-1}\, \Gamma\left(\frac{m+r+1+n}{2}\right) \Gamma\left(\frac{m+r+1-n}{2}\right) \tag{8}$$

Hence μ_r'—the rth moment about the origin is given by

$$\mu_r' = y_0 2^{m+r-1} \Gamma\left(\frac{m+r+1+n}{2}\right) \Gamma\left(\frac{m+r+1-n}{2}\right)$$

Substituting for y_0

$$\mu_r' = 2^r \frac{\Gamma\left(\frac{m+r+1+n}{2}\right) \Gamma\left(\frac{m+r+1-n}{2}\right)}{\Gamma\left(\frac{m+n+1}{2}\right) \Gamma\left(\frac{m-n+1}{2}\right)} \tag{9}$$

From (9) we get the recurrence formula

$$\mu'_{2k+1} = 2^2\left(\frac{m+n}{2}+k\right)\left(\frac{m-n}{2}+k\right)\mu'_{2k-1} \tag{10}$$

and

$$\mu'_{2k+2} = 2^2\left(\frac{m+n+1}{2}+k\right)\left(\frac{m-n+1}{2}+k\right)\mu'_{2k} \tag{11}$$

4. *Distribution of* $v = \frac{x_1}{x_2}$ *where* x_1 *and* x_2 *are distributed according to*

$$\left.\begin{aligned} f(x_1)\,dx_1 &= y_0\, x_1^{m_1} k_{n_1}(x_1)\,dx_1 \\ \phi(x_2)\,dx_2 &= y_0^1\, x_2^{m_2} k_{n_2}(x_2)\,dx_2 \end{aligned}\right\} \tag{12}$$

The distribution of v is given by[7] as

$$dF = dv \int_0^\infty y_0\, y_0^1\, v^{m_1} x_2^{m_1} x_2\, k_{n_1}(vx_2)\, x_2^{m_2} k_{n_2}(x_2)\, dx_2$$

$$= y_0\, y_0^1\, v^{m_1}\, dv \int_0^\infty x_2^{m_1+m_2+1} k_{n_1}(vx_2)\, k_{n_2}(x_2)\, dx_2 \tag{13}$$

It is shown that the value of the integral is[8] with proper change of symbols

$$= 2^{m_1+m_2} v^{n_1} \Gamma(\lambda)\,\Gamma(\mu) \int_0^\infty \frac{x_2^{\nu}\, dx_2}{(v^2+x_2^2)^{\lambda}\,(1+x_2^2)^{\mu}} \tag{14}$$

where $\lambda = \frac{m_1+m_2+n_1-n_2}{2} + 1$

$$\mu = \tfrac{1}{2}(m_1+m_2-n_1+n_2)+1$$

$$\nu = (m_1+m_2)-(n_1+n_2)+1$$

By putting $x_2 = \tan\theta$, the integral in (14) can be expanded in powers of $(1-v^2)$ and we find the value of the integral to be

$$\frac{1}{2}\,\frac{\Gamma\left(\frac{\nu+1}{2}\right)\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{\nu+k}{2}+1\right)}\, F\left(\frac{k+1}{2}, \lambda, \frac{\nu+k}{2}+1, a\right) \tag{15}$$

where $$k = 2\mu + 2\lambda - \nu - 2$$
$$a = 1 - v^2$$

and F is the Hypergeometric Function.

Substituting from (14) and (15) in (13), we get

$$dF = y_0 y_0^1 \, 2^{m_1+m_2-1} \frac{\Gamma(\lambda)\,\Gamma(\mu)\,\Gamma\left(\frac{\nu+1}{2}\right)\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{\nu+k}{2}+1\right)} \times v^{m_1+n_1}\, F\left(\frac{k+1}{2},\ \lambda,\ \frac{\nu+k}{2}+1,\ 1-v^2\right) dv \tag{16}$$

where $y_0 = 1/2^{m_1-1}\,\Gamma\left(\frac{m_1+1+n_1}{2}\right)\Gamma\left(\frac{m_1+1-n_1}{2}\right)$

and $y_0^1 = 1/2^{m_2-1}\Gamma\left(\frac{m_2+1+n_2}{2}\right)\Gamma\left(\frac{m_2+1-n_2}{2}\right)$

(16) is the required distribution of x_1/x_2.

5. *Particular Cases.*—Put $m = u_1 + a_2 - 1$
$$n = a_1 - a_2$$

We have for the distribution (3) the rth moment about the origin, given by

$$\mu_r' = 2^r \frac{\Gamma\left(a_1+\frac{r}{2}\right)\Gamma\left(a_2+\frac{r}{2}\right)}{\Gamma(a_1)\,\Gamma(a_2)} \tag{17}$$

The distribution of $v = \frac{t_1}{t_2}$ is given by, taking $m_1 = m_2 = a_1 + a_2 - 1$, $n_1 = n_2 = a_1 - a_2$ and substituting in (16)

$$dF = \frac{2B(2a_1, 2a_2)}{B^2(a_1, a_2)}\, v^{2a_1-1}\, F(2a_1, a_1+a_2, 2a_1+2a_2, 1-v^2)\, dv \tag{18}$$

where B is the Beta-Function.

In particular put $a_1 = a_2 = \frac{1}{2}(N-1)$ and the constant B (in $t = 2\left(\sqrt{(Z/B)}\right) = 1$.

Then $v = \frac{t_1}{t_2} = \sqrt{\frac{Z_1}{Z_2}}$ is distributed as

$$dF = \frac{2B(2a_1, 2a_1)}{B^2(a_1, a_1)}\, v^{2a_1-1}\, F(2a_1, 2a_1, 4a_1, 1-v^2)\, dv \tag{19}$$

Substituting v for v^2, we get the distribution of $\frac{Z_1}{Z_2}$ as

$$dF = \frac{B(2a_1, 2a_1)}{B^2(a_1, a_1)}\, v^{a_1-1}\, F(2a_1, 2a_1, 4a_1, 1-v)\, dv \tag{20}$$

which is the distribution required to test the hypothesis H_1, where Z_1 and Z_2 are dstributed according to (2).

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ON AN ABSOLUTE CONSTANT IN THE THEORY OF TAUBERIAN SERIES

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1. R. P. Agnew [1] has obtained a theorem on the Abel transform of a Tauberian series of complex terms, substantially improving a result due to H. Hadwiger [2]. By a slight generalisation of Agnew's method, we can prove an exactly similar theorem for the D (λ_n)-transform of the series of complex terms Σa_n:

$$F(s) = \sum_{\nu=1}^{\infty} a_\nu e^{-\lambda_\nu s} \, (s > 0), \; 0 = \lambda_0 < \lambda_1 < \lambda_2 < \ldots, \; \lambda_n \to \infty, \tag{1.1}$$

assuming, in addition to the Tauberian hypothesis:

$$\frac{\lambda_n \, | a_n |}{\lambda_n - \lambda_{n-1}} < K \qquad (n = 1, 2, 3, \ldots), \tag{1.2}$$

the condition

$$\lambda_n - \lambda_{n-1} = O(1) \qquad (n \to \infty). \tag{1.3}$$

In the proof of the D (λ_n)-analogue of Agnew's theorem, we write

$$A(x) = \sum_{\lambda_\nu \leqslant x} a_\nu ; \tag{1.4}$$

and, in its statement, we denote by L the set of limit points, as $x \to \infty$, of $A(x)$ and by $\mathrm{L_D}$ the set of limit points, as $s \to +0$, of $F(s)$.

THEOREM.—*Each of the following assertions* (i), (ii) *is true when* $\rho \geqslant \rho_1$, *while the first is not necessarily true when* $\rho < \rho_1$, ρ_1 *being defined by*

$$\rho_1 = \gamma + \log \log 2 + 2 \int_{\log 2}^{\infty} \frac{e^{-x}}{x} \, dx \tag{1.5}$$

where γ *is Euler's constant.*

(i) *Under conditions* (1.2) *and* (1.3) *to each* z'E L *corresponds a* z''E $\mathrm{L_D}$ *such that*

$$| z' - z'' | \leqslant \rho \limsup_{n \to \infty} \frac{\lambda_n | a_n |}{\lambda_n - \lambda_{n-1}}. \tag{1.6}$$

(ii) *Under conditions* (1·2) *and* (1.3), *to each* z''E $\mathrm{L_D}$ *corresponds a* z'E $\mathrm{L_D}$ *such that* (1·6) *holds.*

2. To prove this theorem we require the three lemmas given below.

LEMMA 1.

$$\lim_{x \to +0} \left[\int_x^\infty \frac{e^{-t}}{t}\, dt + \log x + \gamma \right] = 0.$$

LEMMA 2.—*If $f(x)$ is positive, steadily decreasing, and if the strictly increasing divergent sequence $\{\lambda_n\}$ is subject to condition* (1.3), *i.e., if $\lambda_n - \lambda_{n-1} \leqslant k$, then*

$$\sum_{\nu=1}^{n} (\lambda_\nu - \lambda_{\nu-1}) f(\lambda_\nu) - \int_{\lambda_1}^{\lambda_n} f(x)\, dx$$

converges, as $n \to \infty$, to limit satisfying the inequalities

$$-k f(\lambda_1) \leqslant \lim_{n \to \infty} \left[\sum_{\nu=2}^{n} (\lambda_\nu - \lambda_{\nu-1}) f(\lambda_\nu) - \int_{\lambda_1}^{\lambda_n} f(x)\, dx \right] \leqslant 0. \qquad (2.1)$$

These two lemmas are easily proved by methods indicated elsewhere [1, 3] Using the second lemma we can prove

LEMMA 3.—*The series*

$$\sum_{\nu=2}^{\infty} \int_{\lambda_{\nu-1}}^{\lambda_\nu} \left(\frac{e^{-xs}}{x} - \frac{e^{-\lambda_\nu s}}{\lambda_\nu} \right) dx \equiv \sum_{\nu=2}^{\infty} \phi_\nu(s) \qquad (s > 0),$$

$$\sum_{\nu=2}^{\infty} \int_{\lambda_{\nu-1}}^{\lambda_\nu} \left(\frac{1}{x} - \frac{1}{\lambda_\nu} \right) dx \equiv \sum_{\nu=2}^{\infty} \phi_\nu(0)$$

are convergent, the first to $\Delta(s)$ and the second to C such that*

$$\lim_{s \to +0} \Delta(s) = C. \qquad (2.2)$$

Proof.—The convergence of the series $\Sigma\phi_n(s)$, $\Sigma\phi_n(0)$ is a consequence of the first half of Lemma 2. The prove (2·2) we note that $(e^{-xs} - 1)/x$, $s > 0$, is monotone increasing and therefore

$$\frac{e^{-xs} - 1}{x} \leqslant \frac{e^{-\lambda_\nu s} - 1}{\lambda_\nu} \qquad (\lambda_{\nu-1} \leqslant x \leqslant \lambda_\nu)$$

---

*We can write

$$\int_{\lambda_1}^{\infty} \frac{e^{-xs}}{x}\, dx - \sum_{\nu=2}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} = \Delta(s) \qquad (s > 0)$$

since the integral and the series separately converge.

or
$$\int_{\lambda_{\nu-1}}^{\lambda_\nu}\left(\frac{e^{-xs}}{x}-\frac{e^{-\lambda_\nu s}}{\lambda_\nu}\right)dx < \int_{\lambda_{\nu-1}}^{\lambda_\nu}\left(\frac{1}{x}-\frac{1}{\lambda_\nu}\right)dx.$$

Hence
$$0 < \phi_\nu(s) \leqslant \phi_\nu(0) \qquad (s \geqslant 0)$$

and, by Weierstrass's M-test, $\Sigma\phi_n(s)$ is uniformly convergent for $s \geqslant 0$. The last mentioned fact implies that $\Delta(s)$ is continuous for $s \geqslant 0$ and leads at once to (2.2).

3. *Proof that the asssertions of the theorem hold for* $\rho \geqslant \rho_1$.

Let us write
$$\frac{\lambda_n a_n}{\lambda_n - \lambda_{n-1}} = x_n \tag{3.1}$$

so that, in virtue of (1.2),
$$\limsup_{n\to\infty} |x_n| < \infty.$$

Then we have, from (1.1), (1.4) and (3.1),
$$\begin{aligned} A(\lambda_n) - F(s) &= \sum_{\nu=1}^{n}\frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu}x_\nu - \sum_{\nu=1}^{\infty}\frac{\lambda_\nu-\lambda_{\nu-1}}{\lambda_\nu}e^{-\lambda_\nu s}x_\nu \\ &= \sum_{\nu=1}^{n}\frac{\lambda_\nu-\lambda_{\nu-1}}{\lambda_\nu}(1-e^{-\lambda_\nu s})x_\nu - \sum_{\nu=n+1}^{\infty}\frac{\lambda_\nu-\lambda_{\nu-1}}{\lambda_\nu}e^{-\lambda_\nu s}x_\nu \\ &= \sum_{\nu=1}^{\infty}\alpha_\nu(n,s)\,x_\nu \end{aligned} \tag{3.2}$$

where
$$\alpha_\nu(n,s) = \begin{cases}(\lambda_\nu-\lambda_{\nu-1})(1-e^{-\lambda_\nu s})/\lambda_\nu & (1 \leqslant \nu \leqslant n), \\ -(\lambda_\nu-\lambda_{\nu-1})e^{-\lambda_\nu s}/\lambda_\nu & (\nu > n).\end{cases}$$

And so
$$\begin{aligned}\sum_{\nu=1}^{\infty}|\alpha_\nu(n,s)| &= \sum_{\nu=1}^{n}\frac{\lambda_\nu-\lambda_{\nu-1}}{\lambda_\nu}(1-e^{-\lambda_\nu s}) + \sum_{\nu=n+1}^{\infty}\frac{\lambda_\nu-\lambda_{\nu-1}}{\lambda_\nu}e^{-\lambda_\nu s} \\ &= \sum_{\nu=1}^{n}\frac{\lambda_\nu-\lambda_{\nu-1}}{\lambda_\nu} - \sum_{\nu=1}^{\infty}\frac{\lambda_\nu-\lambda_{\nu-1}}{\lambda_\nu}e^{-\lambda_\nu s} + 2\sum_{\nu=n+1}^{\infty}\frac{\lambda_\nu-\lambda_{\nu-1}}{\lambda_\nu}e^{-\lambda_\nu s} \\ &= \left[1+\int_{\lambda_1}^{\lambda_n}\frac{dx}{x} - \sum_{\nu=2}^{n}\phi_\nu(0)\right] - \left[e^{-\lambda_1 s} + \int_{\lambda_1}^{\infty}\frac{e^{-xs}}{x}dx - \Delta(s)\right] \\ &\quad + 2\left[\int_{\lambda_n}^{\infty}\frac{e^{-xs}}{x}dx - \Delta_n(s)\right] \end{aligned} \tag{3.3}$$

where the first two square-bracketed expresions are obtained by using Lemma 3 and the third expression by a similar method; also $\Delta_n(s)$ is such that $\Delta_1(s) \equiv \Delta(s)$ and, under the condition $\lambda_n - \lambda_{n-1} \leqslant k$,

$$|\Delta_n(s)| \leqslant k e^{-\lambda_n s}/\lambda_n < k/\lambda_n.^{*} \tag{3.4}$$

Using (3.4) in (3.3) and putting $xs = t$ in the three integrals in (3.3), we get

$$\sum_{\nu=1}^{\infty} |a_\nu(n, s)| = (1 - e^{-\lambda_1 s}) + [\Delta(s) - \sum_{\nu=2}^{n} \phi_\nu(0)] - \left[\log \lambda_1 s + \int_{\lambda_1 s}^{\infty} \frac{e^{-t}}{t}\, dt\right] \tag{3.5}$$

$$+ \left[\log \lambda_n s + 2 \int_{\lambda_n s}^{\infty} \frac{e^{-t}}{t}\, dt\right] + O\left(\frac{1}{\lambda_n}\right) \qquad (n \to \infty).$$

Suppose that $n = n(s)$ is chosen so that $\lambda_n s \leqslant \tau < \lambda_{n+1} s$ and therefore $\lambda_n s \to \tau$ as $s \to +0$; and set

$$a_\nu(n(s), s) = \beta_\nu(s),$$

$$\gamma + \log \tau + 2 \int_{\tau}^{\infty} \frac{e^{-t}}{t}\, dt = \mathrm{P}(\tau). \tag{3.6}$$

Then

$$\lim_{s \to +0} \beta_\nu(s) = 0 \qquad (\nu = 1, 2, 3, \ldots). \tag{3.7}$$

Further, as a result of (2.2) and Lemma 1, (3.5) yields, as $s \to +0$,

$$\lim_{s \to +0} \sum_{\nu=1}^{\infty} |\beta_\nu(s)| = \mathrm{P}(\tau). \tag{3.8}$$

Finally (3.2) can be written in terms of s:

$$A(\tau/s) - F(s) = \sum_{\nu=1}^{\infty} \beta_\nu(s)\, x_\nu$$

and this relation, in conjunction with (3.7) and (3.8), leads to

$$\limsup_{s \to +0} |A(\tau/s) - F(s)| \leqslant \mathrm{P}(\tau) \limsup_{n \to \infty} |x_n|. \tag{3.9}$$

The best value of τ in (3·9) is evidently that which makes $\mathrm{P}(\tau)$ minimum. This value is seen to be $\tau = \log 2$ and to correspond to $\mathrm{P}(\tau) = \rho_1$, the number defined in (1.5). Therefore from (3.9) we deduce that

$$\limsup_{s \to +0} |A(\log 2/s) - F(s)| \leqslant \rho_1 \limsup_{n \to \infty} |x_n|. \tag{3·10}$$

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[*] To prove (3·4) we have only to choose $f(x) = e^{-xs}/x$ in (2·1) and the lower limits of summation and integration to be $\nu = n+1$ and λ_n respectively, instead of $\nu = 2$ and λ_1.

To prove that assertions (i) and (ii) are true when $\rho = \rho_1$, consider a limit point of z $A(x)$ [or of $F(s)$]. Then there is a sequence $s_1, s_2, \ldots$ such that $s_\nu \to +0$ and $A(\log 2/s_\nu) \to z$ [or $F(s_\nu) \to z$]. From this and (3.10) we deduce that $F(s_\nu)$ [or $A(\log 2/s_\nu)$] is bounded and therefore there is a subsequence $S_1, S_2, \ldots$ such that $F(S_\nu)$ [or $A(\log 2/S_\nu)$] has a limit w and when $s \to +0$ over the subsequence, (3·10) gives

$$|z - w| \leqslant \rho_1 \limsup_{n \to \infty} \frac{|a_n| \lambda_n}{\lambda_n - \lambda_{n-1}}.$$

Thus assertions (i), (ii) are true for $\rho = \rho_1$ and necessarily so for $\rho > \rho_1$ as well.

4. We can prove that, when $\rho < \rho_1$, assertion (i) is false for a *given* $\{\lambda_n\}$, by means of a Gegenbeispiel modelled on that of Agnew [1, §§ 4, 5] but modified to suit our requirements, in the light of the preceding arguments. The Gegenbeispiel itself rests on Lemma 5 below which in its turn rests principally on Lemma 1 and

LEMMA 4.—*Suppose that* $0 < \epsilon < \frac{1}{2}$, *that* $\mathrm{P}(\tau)$ *is the function defined by* (3·6) *and* $\rho_1 = \mathrm{P}(\log 2)$ *the constant defined by* (1.5). *Then*

$$-\mathrm{P}(\tau) + J(\tau) \equiv -\mathrm{P}(\tau) + \int_{\lambda\tau}^{\infty} \frac{e^{-t}}{t}\, dt < -\rho_1 + K\epsilon + \epsilon$$

when $\lambda > \lambda_0(\epsilon) > 1$, *K being a constant.*

Proof.—The extrema of $-\mathrm{P}(\tau) + J(\tau)$ correspond to the roots of the equation

$$\tau[-\mathrm{P}'(\tau) + J'(\tau)] \equiv -1 + 2e^{-\tau} - \frac{e^{-\lambda\tau}}{\lambda} = 0.$$

As $\lambda \to \infty$, $e^{-\lambda\tau}/\lambda \to 0$ uniformly and the equation has a single root which tends to value $\log 2$. Denoting this root by $\log \overline{2+h}$ we see that $|h| < \epsilon$ when $\lambda > \lambda_1(\epsilon) > 1$; and that the root corresponds to the maximum of $-\mathrm{P}(\tau) + J(\tau)$. Hence

$$-\mathrm{P}(\tau) + J(\tau) \leqslant -\mathrm{P}(\log \overline{2+h}) + \int_{\lambda \log \overline{2+h}}^{\infty} \frac{e^{-t}}{t}\, dt \qquad (|h| < \epsilon),$$

for $\lambda > \lambda_1(\epsilon)$. Further

$$\int_{\lambda \log \overline{2+h}}^{\infty} \frac{e^{-t}}{t}\, dt < \int_{\lambda \log (\frac{3}{2})}^{\infty} \frac{e^{-t}}{t} dt < \epsilon$$

for $\lambda > \lambda_2(\epsilon)$. And therefore, for $\lambda > \max(\lambda_1, \lambda_2)$,

$$-\mathrm{P}(\tau) + J(\tau) < -\mathrm{P}(\log \overline{2 + h}) + \epsilon$$
$$< -\mathrm{P}(\log 2) + K\epsilon + \epsilon$$

which is the conclusion sought.

LEMMA 5.—*Let* $0 < \epsilon_1 < \frac{1}{2}$. *Let* $\Sigma\, a_n$ *be the (real) series*

$$0 + 0 + \ldots + 0 + \xi_p + \sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} - \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} + 0 + 0 + \ldots \tag{4.1}$$

where $\{\lambda_n\}$ *satisfies* (1·3) *in the form* $\lambda_n - \lambda_{n-1} \leqslant k$,

$$\xi_p = -\sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} + \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu}, \tag{4.2}$$

and q, m *are the least integers satisfying*

$$\lambda - \frac{k/2}{\lambda_p} \leqslant \frac{\lambda_q}{\lambda_p} < \lambda + \frac{k/2}{\lambda_p}, \tag{4.3}$$

$$\lambda - \frac{k/2}{\lambda_q} \leqslant \frac{\lambda_m}{\lambda_q} < \lambda + \frac{k/2}{\lambda_q}, \tag{4.4}$$

with reference to p *and a (suitably large)* λ. *Then, we can choose* p, λ, *at the same time fixing* q, m *as in* (4.3), (4.4), *so that the series* Σa_n *in* (4.1) *satisfies the following conditions (in the notation of* §1).

$$A(\lambda_n) < \log \lambda + 2\epsilon_1 \; (n = 1, 2, \ldots), \; A(\lambda_0) > \log \lambda - 2\epsilon_1, \tag{4.5}$$

$$F(s) < 6\epsilon_1 + K_1\epsilon_1 + \log \lambda - \rho_1 \qquad (s > 0). \tag{4.6}$$

Proof.—From (4.2)

$$\xi_p = -\int_{\lambda_p}^{\lambda_q} \frac{dx}{x} + \delta_p + \int_{\lambda_q}^{\lambda_m} \frac{dx}{x} - \delta_q$$

where $|\delta_p| < k/\lambda_p$,* $|\delta_q| < k/\lambda_q$. Hence

$$|\xi_p| \leqslant \log\left(\frac{\lambda_m}{\lambda_q}\Big/\frac{\lambda_q}{\lambda_p}\right) + |\delta_p| + |\delta_q|$$
$$< \log[(\lambda + 2^{-1}\lambda_p^{-1}k)/(\lambda - 2^{-1}\lambda_p^{-1}k)] + |\delta_p| + |\delta_q| \tag{4.7}$$

on account of (4.3) and (4.4).

---

* In the notation of Lemma 3, $\delta_p = \sum_{\nu=p+1}^{q} \phi_\nu(o)$. That $|\delta_p| < k/\lambda_p$ follows from (2.1) before the limit operation provided we take $f(x) = 1/x$ and the lower limits of summation and integration to be $\nu = p + 1$ and λ_p respectively.

Next, the definition of $F(s)$ gives, for our series (4.1),

$$F(s) = 0 + 0 + \dots + 0 + \xi_p e^{-\lambda_p s}$$

$$+ \sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} - \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} + 0 + 0 ..$$

$$= \xi_p e^{-\lambda_p s} + \sum_{\nu=p+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} - 2 \sum_{\nu=q+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s}$$

$$+ \sum_{\nu=m+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s}$$

$$\left.\begin{aligned} &= \xi_p e^{-\lambda_p s} + \int_{\lambda_p}^{\infty} \frac{e^{-xs}}{x}\,dx - \Delta_p(s) - 2\int_{\lambda_q}^{\infty} \frac{e^{-xs}}{x}\,dx + 2\,\Delta_q(s) \\ &\qquad + \int_{\lambda_m}^{\infty} \frac{e^{-xs}}{x}\,dx - \Delta_m(s) \end{aligned}\right\} \tag{4.8}$$

where $|\Delta_n(s)| < k/\lambda_n \ (n = p, q, m)$ from (3.4) and

$$\int_{\lambda_q}^{\infty} \frac{e^{-xs}}{x}\,dx = \int_{\tau}^{\infty} \frac{e^{-t}}{t}\,dt \qquad (\tau = \lambda_q s), \tag{4.9}$$

$$\int_{\lambda_p}^{\infty} \frac{e^{-xs}}{x}\,dx < \int_{\tau/(\lambda + 2^{-1}\lambda_p^{-1}k)}^{\infty} \frac{e^{-t}}{t}\,dt = I^* \quad \text{(say)}, \tag{4.10}$$

$$\int_{\lambda_m}^{\infty} \frac{e^{-xs}}{x}\,dx < \int_{\tau\,(\lambda - 2^{-1}\lambda_p^{-1}k)}^{\infty} \frac{e^{-t}}{t}\,dt = J^* \quad \text{(say)}, \tag{4.11}$$

the last two inequalities being obtained by the use of (4.3) and (4.4). We can first choose p so that

$$|\delta_p| + |\delta_q| + |\Delta_p(s)| + 2\,|\Delta_q(s)| + |\Delta_m(s)| < \epsilon_1 \tag{4.12}$$

and then λ' so that, for $\lambda > \lambda'$,

$$\log(\lambda + 2^{-1}\lambda_p^{-1}k) < \log\lambda + \epsilon_1, \ \log(\lambda - 2^{-1}\lambda_p^{-1}k) > \log\lambda - \epsilon_1, \tag{4.13}$$

$$I^* < \epsilon_1 - \log[\tau/(\lambda + 2^{-1}\lambda_p^{-1}k)] - \gamma \tag{4.14}$$

$$< 2\epsilon_1 + \log\lambda - \log\tau - \gamma, \tag{4.15}$$

appealing to Lemma 1 in justification of (4.14) and then deducing (4.15) form (4.14) by means of (4·13). Further, using (4.13) and (4.12) in (4.7), we see that

$$|\xi_p| < 3\epsilon_1 \qquad (\lambda > \lambda'). \tag{4.16}$$

Also, using (4.9), (4.10), (4.11), (4.15), (4.16) in (4.8), we get

$$F(s) < 5\epsilon_1 + \log\lambda - \mathrm{P}(\tau) + J^* \qquad (\lambda > \lambda') \tag{4.17}$$

while, arguing as in Lemma 4, we can find λ'' such that

$$-\mathrm{P}(\tau) + J^* < -\rho_1 + K_1\epsilon_1 + \epsilon_1 \qquad (\lambda > \lambda''). \tag{4.18}$$

Hence there is a $\lambda > \max(\lambda', \lambda'')$ for which (4.17), (4.18) both hold and together give rise to (4.6).

It remains to prove (4.5). For this purpose, we have only to recall that, as a result of (4.4),

$$A(\lambda_n) \leqslant \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} \qquad (n = 1, 2, 3, \ldots)$$

$$= \int_{\lambda_q}^{\lambda_m} \frac{dx}{x} - \delta_q < \log(\lambda + 2^{-1}\lambda_p^{-1}k) + \epsilon_1 \qquad (\lambda > \lambda'),$$

$$A(\lambda_q) = \int_{\lambda_q}^{\lambda_m} \frac{dx}{x} - \delta_q > \log(\lambda - 2^{-1}\lambda_p^{-1}k) - \epsilon_1 \qquad (\lambda > \lambda'),$$

and then appeal to (4.13). This concludes the proof of Lemma 5.

It is obvious, but relevant to the sequel, that the series Σa_n in (4.1) satisfies the conditions

$$\limsup_{n\to\infty} \frac{\lambda_n |a_n|}{\lambda_n - \lambda_{n-1}} = 1, \ \lim_{n\to\infty} A(\lambda_n) = 0.$$

5. *Proof that, when $\rho < \rho_1$, assertion* (i) *is false.* This may be based on the fact that it is easy to adapt the reasoning of Agnew [1, §5] to a series constructed as follows.

Denote the series Σa_n of Lemma 5 by $\Sigma a_p(n)$; and its D(λ_n)-transform by $F_p(s)$. Choose an increasing sequence of integers $p_1, p_2 \ldots.$ (with $p_1 = p$ and λ as in Lemma 5) so that associated with it there is a positive decreasing null sequence $s_1, s_2, \ldots.$ satisfying the following conditions for each $r = 1, 2, \ldots.$

$$\lambda_{p_{r+1}} > (\lambda + 2^{-1}\lambda_{p_1}^{-1}k)^2 \lambda_{p_r},$$

$$\sum_{j=1}^{r} |F_{p_j}(s)| < \epsilon_1 \qquad (0 < s \leqslant s_r),$$

$$\sum_{\nu=p_{r+1}}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} < \epsilon_1 \qquad (s > s_r).$$

It is readily verified that such a choice of $\{p_r\}$ and $\{s_r\}$ is possible and (by the use of Lemma 5) that the series obtained by the termwise addition of $\Sigma a_{p_1}(n), \Sigma a_{p_2}(n), \ldots,$ falsifies assertion (i) of the theorem in §1 for $\rho < \rho_1$.

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AZOIC DYES*

Part IX. The Behaviour of ω-Benzoyl-2-acetyl-1-naphthol towards Diazonium Salts

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The members of the Naphtol AS series derived from 2-hydroxy-3-naphthoic acid and similar *o*-hydroxycarboxylic acids yield orange, red and deeper colours. The attachment of an arylazo group to a carbon atom in an aliphatic group being one method for preparing yellow dyes, the I.G. in 1921 introduced Naphtol AS–G, which is bisacetoacet-*o*-tolidide, as a "naphthol" for the production of yellow shades; coupled on the fibre with diazotised chloranilines lemon-yellow shades could be obtained. The poor substantivity and the moderate light fastness of the Naphtol AS–G shades then led to the introduction of Naphtol AS–LG, L_3G and L_4G, the constitution of which has been elucidated by Desai and Mehta.[1] The first two are arylides of terephthaloyl diacetic acid and the last is 2-acetoacetamido-6-ethoxybenzthiazole. With specified diazonium salts the bright yellow shades from Naphtol AS–L_4G possess very high light fastness. It is to be noted, however, that on account of its adequacy for general purposes Naphtol AS–G continues to be widely used for dyeing yellow azoic shades.

The present work is an investigation of the utility, as azoic coupling components, of diketones prepared by the action of sodamide,[2] potassium carbonate[3] or sodium ethoxide[4] on *o*-benzoyloxyaryl methyl ketones. A substance such as 2-benzoylacetyl-1-naphthol (I) has two coupling positions, and the comparative reactivity of these sites for diazonium couplings is of interest. Further, the introduction of a 1:3-diketone group in a dye or a 2-hydroxy-3-naphthanilide type of coupling component might offer a useful method for modifying shades.

2-Benzoylacetyl-1-naphthol (I) was obtained by the action of anhydrous potassium carbonate in toluene on 2-acetyl-1-naphthol benzoate in very good yield.[3] The diketone (I) gave weak dyeings when used as a "naphthol" and coupled with diazotised Fast Red Base B (5-nitro-*o*-anisidine) and Scarlet Base GG (2:5-dichloroaniline); the shades lacked fastness to soaping and light. Treatment of the dyeings with potassium dichromate and copper sulphate did not improve the fastness.

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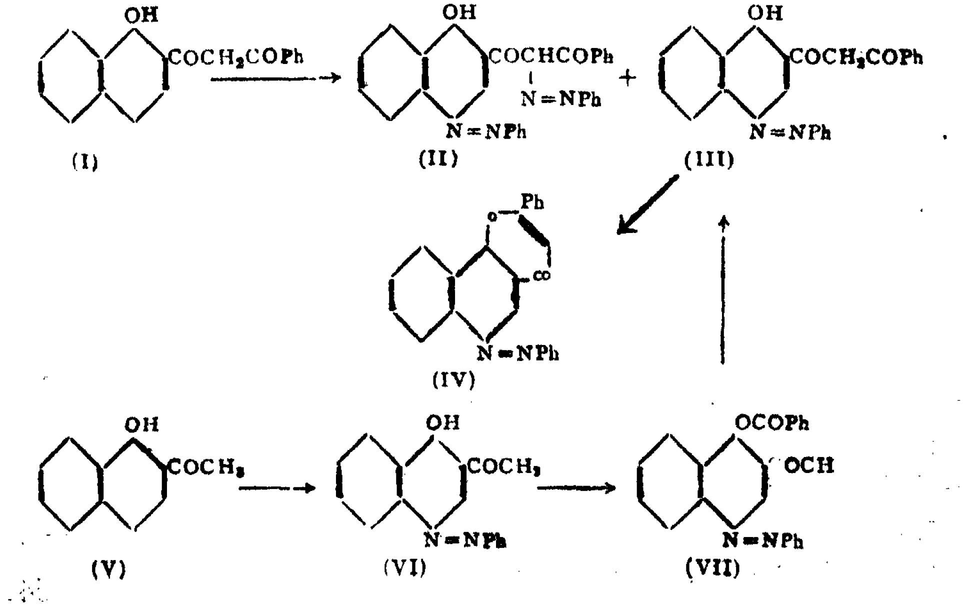
* The earlier papers of this series have appeared as "Studies in the Naphtol AS series" (for Part VIII, see *J. Sc. Ind. Res.*, 1945, 3, 447).

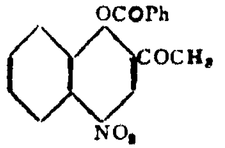
The diketone (I), when coupled in substance with one or more moles of diazotised aniline in alcoholic sodium hydroxide solution, yielded the disazo dye (II). Coupling in alcoholic sodium carbonate or pyridine solution with diazotised aniline (1 mole) yielded a mixture of the disazo dye (II) and a monoazo dye (III), which were separated by careful fractional crystallisation from acetic acid, the latter being less soluble. It was observed that boiling the monoazo dye (III) with acetic acid for a long time during crystallisation yielded a third product, which was ultimately found to be the corresponding flavone (IV). The monoazo dye (III), when dyed as a 'naphthol', and developed with diazotised Fast Red Salt B, gave brown shades which bled considerably during soaping.

The disazo dye was unaffected by treatment with concentrated sulphuric acid in the cold, while the monoazo dye, either by treatment with concentrated sulphuric acid in the cold or by refluxing with glacial acetic acid gave the flavone (IV) by cyclisation. In view of the ring closure taking place only in the case of the monoazo dye, it is evident that the coupling must have taken place in the 4-position. However, to confirm the constitution of the monoazo dye as (III), it was also prepared by an unambiguous method. 2-Acetyl-1-naphthol (V) was coupled with diazotised aniline to obtain 4-benzeneazo-2-acetyl-1-naphthol (VI). Condensation of (VI) with ethyl benzoate in presence of sodium, sodium ethoxide or sodamide was not successful. The benzoate (VII), prepared under the conditions specified, readily underwent rearrangement with potassium carbonate in toluene, and

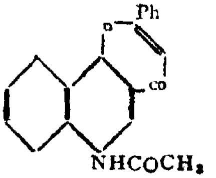


gave 4-benzeneazo-2-benzoylacetyl-1-naphthol (III) identical with the monoazodye obtained by coupling (I) with diazotised aniline. It was observed that 4-nitro-2-acetyl-1-naphthol benzoate (VIII), prepared by the benzoylation of 4-nitro-2-acetyl-1-naphthol, did not undergo rearrangement to the corresponding diketone under these conditions.

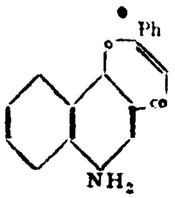
The benzeneazo-naphtha flavone (IV) on reduction with acetic acid and zinc dust, gave the acetamido derivative (IX). Even when the reduction was carried out in a large volume of alcohol with the addition of 1–2 moles of acetic acid, the acetamido derivative (IX), and not the amine (X), was obtained. Reduction with iron and hydrochloric acid in alcoholic solution gave amorphous red products. The deacetylation of (IX) proved difficult since it remained unaffected when treated either with 30 per cent. hydrochloric acid or 10 per cent. sodium hydroxide solution. The aminoflavone (X) could however be very readily obtained by reduction of (IV) by hydrogen under pressure in presence of Raney nickel. When the diketone (III) was reduced under these conditions, the corresponding amine could not be isolated since it was very unstable. However, when (III) was reduced with sodium hydrosulphite in alcoholic alkali, the aminoflavone (X) was obtained, reduction of the azo-group and cyclisation of the diketone taking place simultaneously.



(VIII)



(IX)

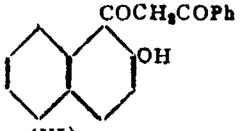


(X)

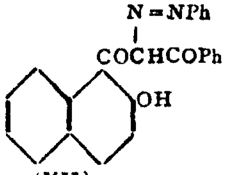
When the diketone (I) was coupled with diazotised 2:5-dichloroaniline (1 mole.) in pyridine or alcoholic sodium hydroxide solution, it gave the disazodye (II; $C_6H_3Cl_2$ instead of Ph). However, coupling in alcoholic sodium carbonate solution with diazotised 2:5-dichloroaniline (1 mole.) gave the disazo dye (II; $C_6H_3Cl_2$ instead of Ph), together with about 5 per cent. of the monoazo dye (III; $C_6H_3Cl_2$ instead of Ph), which was isolated as the flavone (IV; $C_6H_3Cl_2$ instead of Ph). The same monoazo dye was also obtained by the rearrangement of (VII; $C_6H_3Cl_2$ instead of Ph) with potassium carbonate in toluene.

In order to prepare a diketone which does not have a nuclear site for coupling as in (I), ω-benzoyl-1-acetyl-2-naphthol (XI) was prepared by the rearrangement of 1-acetyl-2-naphthyl benzoate with sodium ethoxide.[4]

The diketone (XI) when coupled in sodium hydroxide solution with diazotised aniline gave a red substance, which appeared to be a mixture of the desired azo dye (XII) and 1-benzeneazo-2-naphthol. 1-Acetyl-2-naphthol undergoes a similar displacement on treatment with diazonium salts.[5] Application of (XI) in azoic dyeing by the normal process of impregnation from an aqueous alkaline solution was not possible. The diketone (XI) coupled readily in alcohol-sodium acetate solution and gave ω-benzoyl-ω-benzeneazo-1-acetyl-2-naphthol (XII); but on account of the influence of alcohol in lowering the substantivity of the diketone towards cellulose, a very weak yellow shade, loose to soaping, was obtained when (XI) was applied to cotton yarn from an alcoholic sodium acetate solution and developed with diazotised 2: 5-dichloroaniline.

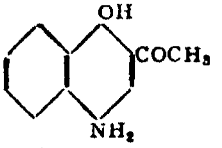


(XI)



(XII)

With a view to studying the effect of a benzamido group *p*- to the hydroxyl in the diketone (I), the synthesis of (XV) was then undertaken. 4-Benzamido-1-naphthol did not undergo the Nencki reaction to give the 2-acetyl compound, from which (XV) could be prepared. The azo dye from acetonaphthol and diazotised metanilic acid was reduced by alkaline sodium hydrosulphite to give the aminonaphthol (XIII), which on treatment with excess of benzoyl chloride gave the dibenzoyl derivative (XIV). Rearrangement of (XIV) with potassium carbonate in toluene gave the diketone (XV). As a "naphthol" (XV) gave a pink shade with diazotised α-aminoanthraquinone, which was loose to soaping and had a light fastness of only



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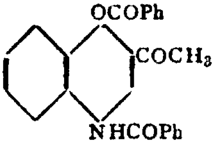

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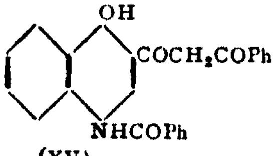

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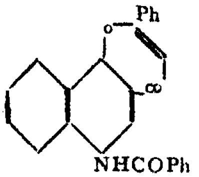

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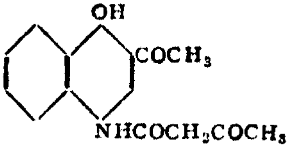
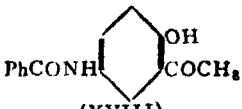


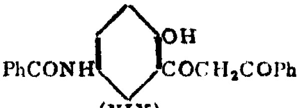
(XVII)

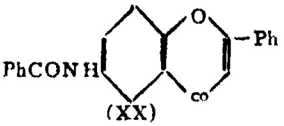
2-3. The diketone (XV) on treatment with concentrated sulphuric acid in the cold gave 6-benzamido-7:8-benzoflavone (XVI).

Condensation of (XIII) with ethyl acetoacetate gave (XVII); the yellowish brown shades produced by development with diazonium salts had poor fastness to light.

5-Benzamido-2-hydroxyacetophenone (XVIII) was prepared by the Fries migration of 4-benzamidophenyl acetate. The benzoate of (XVIII) on treatment with sodamide in benzene gave the diketone (XIX). The diketone was not substantive to cotton, and when developed with diazotised dichloroaniline, it gave a weak brown shade with poor light fastness. The diketone (XIX) could be cyclized as usual to 6-benzamido-flavone (XX).


(XVIII)


(XIX)


(XX)

EXPERIMENTAL

2-*Benzoylacetyl*-1-*naphthol* (*I*)

2-Acetyl-1-naphthyl benzoate (15 g.), toluene (75 c.c.) and freshly ignited potassium carbonate (45 g.) were refluxed under stirring for 8 hours. The deep orange potassium salt was filtered and treated with dilute acetic acid. The diketone (12 g.) crystallised from acetone in bright orange needles, m.p. 147° (Mahal and Venkataraman,[8] 147°).

Coupling of the diketone (*I*) *with diazotised aniline*

The diketone (1·5 g.) was pasted with 10% sodium hydroxide solution (10 c.c.) and dissolved in alcohol (50 c.c.). The solution was diluted with water (10-15 c.c.) and after adding sodium acetate (4 g.), cooled to 0° and coupled with aniline (1·5 g., 3 mols.) in hydrochloric acid (4·5 c.c.) diazotised with sodium nitrite (1·2 g.). The bright red dye (2·1 g.) crystallized from acetic acid in thin, elongated plates, m.p. 168-70° (Found: N, 11·2 $C_{31}H_{22}O_3N_4$ requires N, 11·2%). A little more of the disazo dye was obtained from the filtrate by acidification. The substance also crystallises from the same solvent in a second form with m.p. 204-5°. It gives a brown colour with ferric chloride and a deep cherry red colour with concentrated sulphuric acid. The dye was recovered unchanged from its solution in concentrated sulphuric acid, no cyclization to a flavone taking place under the usual conditions.

When the diketone was coupled under similar conditions using one mole of diazotised aniline, the dye that separated out proved to be (II). The filtrate on acidification gave a sticky substance, which dissolved in concentrated sulphuric acid with a bright green fluorescence, indicating the presence of unreacted diketone.

When the diketone (I) (0·5 g.) in 10% sodium carbonate solution (10 c.c.), alcohol (100 c.c.) and sodium acetate (1 g.), was coupled with diazotised aniline (1 mol.) and stirred for one hour, a deep red solution was obtained which was acidified with dilute hydrochloric acid and the orange red dye collected (0·6 g.). The dye was taken up in acetic acid (20 c.c.), heated to about 110° and the resulting mixture was filtered immediately. The residue (0·2 g.) crystallised from alcohol-acetic acid mixture in thin short orange rods, m.p. 201–2° (Found: N, 7·3. $C_{25}H_{18}O_3N_2$ requires N, 7·2%). The monoazo dye gives a brown colour with ferric chloride and a cherry red colour with concentrated sulphuric acid. From the acetic acid mother-liquors, the disazo dye (II), m.p. 168–70°, was recovered.

The diketone (I) (0·5 g.) was then dissolved in pyridine (20 c.c.) and coupled with one mol. of diazotised aniline. The dark red solution, on dilution and acidification with hydrochloric acid, gave an orange red dye, which could be separated into mono- (III) and disazo (II) dyes as in the previous case; about 0·12 g. of the pure monoazo and 0·1 g. of the disazo dye were obtained.

4-*Benzeneazo*-2-*acetyl*-1-*naphthol* (*VI*)

The bright red dye, prepared in the usual manner from acetonaphthol and diazobenzene chloride, crystallised from acetic acid or chlorobenzene in reddish orange needles, m.p. 143° (Found: N, 9·8. $C_{18}H_{14}O_2N_2$ requires N, 9·7%). It gives a deep brown colour with ferric chloride and a violet colour with concentrated sulphuric acid.

4-*Benzeneazo*-2-*acetyl*-1-*naphthyl benzoate* (*VII*)

The dye (VI) (2 g.), pyridine (10 c.c.) and benzoyl chloride (1·5 g.) were refluxed for six hours in the oil-bath at 140°. The solution was poured over crushed ice and hydrochloric acid. The dark red sticky product was taken up in ether, washed with ice-cold dilute hydrochloric acid, water, and finally with ice-cold sodium carbonate solution. Removal of the solvent and crystallisation from alcohol gave orange prismatic needles (1·7 g.), m.p. 153° (Found: N, 7·1. $C_{25}H_{18}O_3N_2$ requires N, 7·2%).

4-*Benzeneazo*-2-*benzoylacetyl*-1-*naphthol* (*III*)

A mixture of the benzoate (1 g.), toluene (20 c.c.) and potassium carbonate (4 g.) was refluxed for 8 hours. The dark red potassium salt was filtered, washed with benzene and decomposed with dilute acetic acid. The brownish red diketone (0·65 g.) crystallised from acetic acid or alcohol-acetic acid in short orange rods, m.p. 201–2° (Found: N, 7·4. $C_{25}H_{18}O_3N_2$ requires N, 7·2%). A mixed m.p. with the monoazo dye (III) obtained by direct coupling of the diketone showed no depression.

6-*Benzeneazo*-7 : 8-*benzoflavone* (*IV*)

4-Benzeneazo-2-benzoylacetyl-1-naphthol (III) (0·2 g.) was refluxed with glacial acetic acid for 30 minutes, and cooled. The flavone (IV) crystallised in shining yellow needles, m.p. 271° (Found: N, 7·2. $C_{25}H_{16}O_2N_2$ requires N, 7·4%). The substance does not give a ferric chloride colour and is insoluble in aqueous or alcoholic alkali.

Treatment of the dye (III) with cold concentrated sulphuric acid also yielded the same flavone (IV).

4-*Nitro*-2-*acetyl*-1-*naphthyl benzoate* (*VIII*)

4-Nitro-2-acetyl-1-naphthol (2·5 g.), prepared by the nitration of 2-acetyl-1-naphthol with 40% nitric acid at room temperature, pyridine (15 c.c.) and benzoyl chloride (1·5 c.c.) were heated on the water-bath for 30 minutes and the solution poured over ice and hydrochloric acid. The semi-sticky solid which separated was taken up in ether washed with dilute hydrochloric acid, water and cold sodium carbonate solution respectively, the ether extract dried and the solvent removed. The semi-sticky solid crystallised from alcohol in short colourless plates (1·5 g.), m.p. 126–27° (Found: N, 4·0. $C_{19}H_{13}O_5N$ requires N, 4·2%).

6-*Acetamido*-7 : 8-*benzoflavone* (*IX*) was obtained by reduction of the flavone (IV) with zinc dust in acetic acid solution. It crystallised from acetic acid in small lustrous, yellow needles, which melted with darkening in colour at 306–7° (Found: N, 4·3. $C_{21}H_{15}O_3N$ requires N, 4·2%).

6-*Amino*-7 : 8-*benzoflavone* (*X*)

(i) The benzeneazoflavone (IV) (0·5 g.) was suspended in alcohol (30 c.c.), Raney nickel catalyst added and shaken with hydrogen under pressure (40 lbs.) for two hours when the flavone slowly went into solution. The catalyst was filtered off and the yellow filtrate diluted with water, the product which separated (0·25 g.) crystallised from alcohol in long, shining yellow needles, m.p. 220° (Found: N, 4·6. $C_{19}H_{13}O_2N$ requires N, 4·8%). It dissolves in concentrated sulphuric acid giving a colourless solution with a bright bluish violet fluorescence.

(ii) The dye (III) (0·1 g.), dissolved in alcohol (20 c.c.) and 10% sodium hydroxide solution (1 c.c.) was warmed to about 70°, and reduced by sodium hydrosulphite till the colour of the solution changed from deep red to yellowish red. After heating for a few minutes, the solution was acidified with dilute acetic acid, concentrated and cooled. The aminoflavone (X) crystallised from alcohol in long, shining yellow needles.

Coupling of the diketone (I) with diazotised 2: 5-*dichloroaniline*

The diketone (I) (0·5 g.), dissolved in pyridine (20 c.c.) was coupled in the usual manner with one mole. of diazotised 2: 5-dichloroaniline. The dye, precipitated by dilution and acidification with hydrochloric acid, crystallised from acetic acid in fluffy aggregates of red needles (0·2 g.), m.p. 215–16° (Found: N, 8·9. $C_{31}H_{18}Cl_4O_3N_4$ requires N, 8·9%). The disazo dye (II; $C_6H_3Cl_2$ instead of Ph) gives a light brown colour with ferric chloride. The filtrate, after separation of the disazo dye, on dilution and crystallisation, gave the unreacted diketone (0·2 g.).

The diketone (I) (0·5 g.) dissolved in alcoholic sodium carbonate solution was then coupled with one mol. of diazotised 2: 5-dichloroaniline. The dye was boiled in acetic acid (50 c.c.) and a small quantity of a yellowish-orange solid which separated was immediatey filtered off. It crystallised from a large volume of acetic acid in thin yellow rods (30 mg.), m.p. 295–96° (Found: N, 6·4. $C_{25}H_{14}Cl_2O_2N_2$ requires N, 6·2%). It does not give any ferric chloride colour and is not soluble in aqueous or alcoholic alkali. Analysis and its properties indicated that it was the flavone (IV, $C_6H_3Cl_2$ instead of Ph). From the acetic acid mother liquor, the disazo dye (0·2 g.) was obtained.

4-(2′: 5′-*Dichloro*)-*benzeneazo*-2-*acetyl*-1-*naphthol* (*VI*; $C_6H_3Cl_2$ *instead of Ph*).

Acetonaphthol was coupled with diazotised 2: 5-dichloroaniline, and the red dye crystallised from chlorobenzene in long needles, m.p. 229–30° (Found: N, 8·1. $C_{18}H_{12}Cl_2O_2N_2$ requires N, 7·8%).

4-(2′: 5′-*Dichloro*)-*benzeneazo*-2-*acetyl*-1-*naphthyl benzoate* (*VII*; $C_6H_3Cl_2$ *instead of Ph*)

The dye (VI; $C_6H_3Cl_2$ instead of Ph) was benzoylated by refluxing with benzoyl chloride in pyridine. The benzoate crystallised from alcohol in yellowish orange needles, m.p. 184–5° (Found: N, 6·1. $C_{25}H_{16}Cl_2O_3N_2$ requires N, 6·0%).

6-(2′: 5′-*Dichloro*)-benzeneazo-7: 8-*benzoflavone* (*IV*; $C_6H_3Cl_2$ *instead of Ph*)

The benzoate on treatment with potassium carbonate in toluene rearranged to the yellowish red diketone (III; $C_6H_3Cl_2$ instead of Ph), m.p. 238–40°, which was converted into the corresponding flavone (IV; $C_6H_3Cl_2$

tnsead of Ph) by treatment with boiling glacial acetic acid, when it crystallised in thin yellow rods, m.p. 295–96° (Found: N, 6·3. $C_{25}H_{14}Cl_2O_2N_2$ requires N, 6·2%), identical with the corresponding flavone obtained by direct coupling of the diketone with diazotised 2:5-dichloraniline followed by treatment with acetic acid.

*ω-Benzeneazo-ω-benzoyl-*1*-acetyl-*2*-naphthol (XII)*

The diketone (XI) (0·3 g.), prepared by the rearrangement of 1-acetyl-2-naphthol benzoate with sodium ethoxide,[4] was dissolved in alcohol (20 c.c.) and sodium acetate (1 g.) added, when the solution became greenish in colour. The solution was cooled and coupled with one mol. of diazotised aniline. The orange dye was filtered (0·3 g.), which crystallised from alcohol in small orange plates, m.p. 162° (Found: N, 7·2. $C_{25}H_{18}O_3N_2$ requires N, 7·2%). It gives a deep brown colour with ferric chloride.

4*-Amino-*2*-acetyl-*1*-naphthol (XIII)*

2-Acetyl-1-naphthol (5 g.) was dissolved in aqueous sodium hydroxide solution and coupled with diazotised metanilic acid (5 g.). The deep red coloured alkaline solution of the dye was heated to 70°, and hydrosulphite (9 g.) was slowly added till the colour of the solution became pale yellow. The orange crystalline amine which separated (3·5 g.) crystallised from dilute alcohol in orange needles, m.p. 122–23° (Found: N, 6·9. $C_{12}H_{11}O_2N$ requires N, 7·0%). It gave a brown colouration with ferric chloride.

4*-Benzamido-*2*-acetyl-*1*-naphthyl benzoate (XIV)*

4-Amino-2-acetyl-1-naphthol (XIII) (3 g.) in pyridine (10 c.c.) was mixed with benzoyl chloride (6 c.c.) and refluxed for 30 minutes. The yellow product (3 g.), obtained on stirring the solution into dilute hydrochloric acid, crystallised from alcohol in colourless needles, m.p. 175–6° (Found: N, 3·2. $C_{26}H_{19}O_4N$ requires N, 3·4%).

4*-Benzamido-*2*-benzoylacetyl-*1*-naphthol (XV)*

(XIV) (1 g.), anhydrous potassium carbonate (4 g.) and benzene (15 c.c.) were refluxed for 8 hours, the orange potassium salt filtered and stirred into dilute acetic acid and the product which separated was filtered. It crystallised from glacial acetic acid in orange needles, m.p. 232° (Found: N, 3·2. $C_{26}H_{19}O_4N$ requires N, 3·4%).

6-Benzamido-α-naphthaflavone (XVI), obtained by treatment of (XV) with cold concentrated sulphuric acid, crystallised from glacial acetic acid in plates, m.p. 273° (Found: N, 3·2. $C_{26}H_{17}O_3N$ requires N 3·6%).

4-*Acetoacetamido*-2-acetyl-1-naphthol (XVII)

4-Amino-2-acetyl-1-naphthol (XIII) (3 g.) and acetoacetic ester (3 c.c.) were refluxed for 6½ hours in chlorobenzene (25 c.c.) with a few drops of one N caustic soda solution. The residue, after distilling off chlorobenzene, was dissolved in caustic soda and reprecipitated by acid. The product (1·5 g.) crystallised from alcohol (Norit) in long yellow needles, m.p. 183°. (Found: N, 4·6. $C_{16}H_{15}O_4N$ requires N, 4·9%). It gives a dark green colour with ferric chloride.

2-*Acetyl-4-benzamidophenol* (*XVIII*)

4-Benzamidophenyl acetate (7 g.) was dissolved in dry acetylene tetrachloride (70 c.c.), aluminium chloride (10 g.) added and the mixture heated for 2 hours at 140–45°. The solution was stirred into ice and hydrochloric acid and carbon tetrachloride steam distilled. The yellow product (4 g.) crystallised from alcohol (Norit) in colourless needles, m.p. 155°. (Found: N, 5·2. $C_{15}H_{13}O_3N$ requires N, 5·5%). It gives a blue colour with ferric chloride.

ω-Benzoyl-2-hydroxy-5-benzamidoacetophenone (*XIX*)

2-Acetyl-4-benzamidophenyl benzoate was obtained by refluxing (XVIII) for 1½ hours with benzoyl chloride in pyridine. It crystallised from alcohol in colourless needles, m.p. 168–69° (Found: N, 3·8. $C_{22}H_{17}O_4N$ requires N, 3·9%).

2-Acetyl-4-benzamidophenyl benzoate (4·6 g.), benzene (100 c.c.) and sodamide (5 g.) were refluxed for 4 hours and the yellow product that separated was treated with dilute hydrochloric acid. It crystallised from glacial acetic acid in yellow needles, m.p. 210°. (Found: N, 3·8. $C_{22}H_{17}O_4N$ requires N, 3·9%). It gives an olive brown colour with ferric chloride.

The flavone (XX), obtained by treatment of the diketone (XIX) with cold concentrated sulphuric acid, crystallised from alcohol in colourless plates, m.p. 291° (Found: N, 4·1. $C_{22}H_{15}O_3N$ requires N, 4·1%).

SUMMARY

The utility, as azoic coupling components, of diketones prepared by the action of sodamide and similar reagents on *o*-benzoyloxyaryl methyl ketones has been investigated. 2-Benzoylacetyl-1-naphthol gives weak dyeings when used as a "naphthol" for impregnation of cotton, and development with diazonium salts. The shades lacked fastness to soaping and light. On coupling the diketone in substance with diazonium salts, mono- and disazo dyes were obtained; the constitution of the former, which could

have two possible structures, has been proved to be 4-benzeneazo-2-benzoylacetyl-1-naphthol by an unambiguous synthesis from 4-benzeneazo-2-acetyl-1-naphthol through the corresponding benzoate. The monoazo dye from 1-benzoylacetyl-2-naphthol has been prepared. 4-Benzamido-2-benzoylacetyl-1-naphthol and 4-acetoacetamido-2-acetyl-1-naphthol have also been studied as " naphthols ".

We are grateful to Imperial Chemical Industries (Dyestuffs Group) and to the Sir Dorab Tata Trust for the award of research fellowships to two of us. We are also thankful to Mr. T. S. Gore for carrying out the microanalyses.

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CHEMOTHERAPY OF BACTERIAL INFECTIONS

XII. Synthesis of Some Sulphanilamide and Sulphone Derivatives of Thiazole

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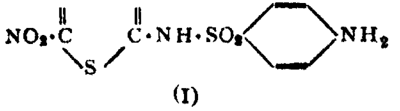
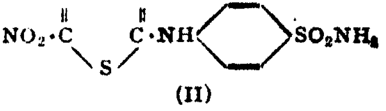
As a sequel to the discovery of the remarkable therapeutic properties of 2-sulphanilamidothiazole, we undertook the synthesis and study of all possible sulphanilamido derivatives of thiazole. Derivatives of 2-sulphanilamidothiazole with alkyl substituents at the positions 4 and 5 of thiazole and N^3 of the tautomeric thiazoline have previously been reported from this laboratory.[1] Herein we report the synthesis and study of more derivatives of this group, which were completed many years ago.

The condensation of acetsulphanilylchloride with 2-amino-5-nitrothiazole[2] and 2-amino-4-methyl-5-nitrothiazole[2] to obtain the 2-acetsulphanilamido derivatives could not be effected. To obtain this compound by the alternative method, 2-bromo-5-nitro-thiazole[3] was condensed with sulphanilamide in the presence of potassium carbonate and copper powder, a condition under which only the sulphonamide grouping has been established to react.[4] The reaction in this case was unusually vigorous. Of the numerous experiments tried under a variety of conditions, the required 2-sulphanilamido-5-nitrothiazole (I) could be isolated in only one experiment in bad yield. The use of acetyl sulphanilamide in the place of sulphanilamide in the above reaction did not lead to any better results. On the other hand, the condensation of 2-bromo-5-nitrothiazole with sulphanilamide in alcoholic solution, a condition under which the amino group is known to react,[4] furnished the isomeric product (II) in good yields.

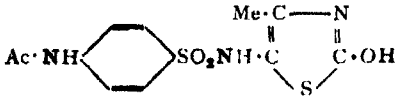


(I)



(II)

In the pyridine series, the three possible isomeric compounds with the sulphanilamido radical substituted at the positions 2, 3 and 4 of the pyridine ring have been synthesised and studied.[5] In the pyrimidine series also, the 2, 4 and 5 substituted sulphanilamido derivatives have been synthesised and studied.[6] But at the time the present work was started, the sulphanilamido derivatives of thiazole substituted in positions 4 and 5 were not known. Arnold and Scaife[7] reported the synthesis of 5-sulphanilamidothiazole starting from chrysean. Jensen and Hansen[8] reported independently the synthesis of 2:4-dimethyl-5-sulphanilamidothiazole. We have attempted the synthesis of a number of 4- and 5-sulphanilamido derivatives. 2-Hydroxy-4-methyl-5-aminothiazole[2] condensed with acetsulphanilylchloride to yield 2-hydroxy-4-methyl-5-acetsulphanilamidothiazole (III) but this could not be deacetylated to the corresponding sulphanilamido derivative. 2:4-Dimethyl-5-amino-thiazole[3] condensed with acetsulphanilylchloride to yield 2:4-dimethyl-5-acetsulphanilamidothiazole (IV, R = Ac.), whose melting point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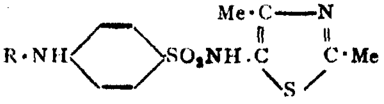
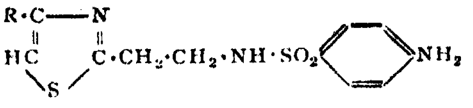

(IV)

does not agree with that given by Jensen and Hansen[8]; however, the deacetylated sulphanilamido derivative (IV, R = H) has the same melting point as that given by Jensen and Hansen. Contrary to the property of the 2-acetsulphanilamidothiazoles, the 5-acetsulphanilamidothiazole derivative is soluble in dilute acid. 2:4-Dimethyl-5-sulphanilamidothiazole has been tested in experimental Pneumococcal (Type I) and *P. pestis* infections in mice; it has about the same activity as sulphathiazole but it shows some peculiar toxic symptoms. The results of these experiments will be published elsewhere.

A few derivatives in which sulphanilamide radical is attached to the thiazole ring through one or two carbon atoms were prepared. Synthesis of such derivatives in the pyridine series have been reported[9] but there is no information available on their therapeutic properties. 2-Methylthiazole and 2:4-dimethylthiazole condensed with sulphanilamide in the presence of formalin to yield the two compounds V, R = H and Me respectively. Since the amino group is free in both these compounds (as revealed by the diazo-reaciton), the condensation has taken place through the sulphonamide radical. In the case of 2:4-dimethylthiazole, the 4-methyl group is established to be inert[13] and so the formula V is assigned to the condensation product. 2-Hydroxy-4-methylthiazole similarly reacted with sulphanilamide in the presence of formalin and the compound obtained is assigned the structure (VI) in view of the known behaviour of the thiazole derivatives.[14] None of these compounds showed any significant therapeutic activity in experimental Pneumococcal (Type I) infections in mice,



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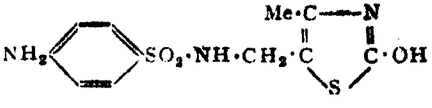

(VI)

p-Aminophenylsulphones of thiazole have previously been studied.[10] Herein the nature of the substituent has been found to influence the therapeutic activity. So by condensing *p*-acetaminobenzenesulphinic acid with 2-halogenothiazole derivatives a number of sulphones have been prepared which are described in the experimental portion. But none of them has been found to be of any value in experimental pneumococcus or plague infections in mice.

EXPERIMENTAL

2-*Sulphanilamido*-5-*nitrothiazole* (I).—An intimate mixture of 2-bromo-5-nitrothiazole (1 g.), sulphanilamide (0·9 g.), anhydrous potassium carbonate (·35 g.) and copper powder (0·3 g.) was heated at 100°. The reaction was unusually vigorous and was over in a few minutes. The dark coloured reaction product was powdered and extracted with boiling water. The deep red aqueous extract yielded nothing on neutralisation. The residual solid was then extracted with hot alcohol which yielded about 0·3 g. of yellow solid which did not crystallise but was purified by dissolving in dilute alkali, or ammonia, and then neutralising with acid; m.p. 245° (Found: N, 18·31. $C_9H_8O_4N_4S_2$ requires N, 18·67%). The presence of a free amino group in this compound was established by the diazo reaction.

2-(*N*^{4}-*Sulphanilamido*)-5-*nitrothiazole* (*II*).—2 - Bromo - 5 - nitrothiazole (4·2 g.) and sulphanilamide (3·45 g.) were refluxed in alcohol (25 c.c.) for 30 minutes. On cooling, deep yellow crystals separated which were collected and dried (yield, 4 g.). A further quantity of 1·7 g. was recovered from the filtrate. On recrystallisation from alcohol or glacial acetic acid, it had m.p. 258–9° (Found: N, 18·38. $C_9H_8N_4O_4S_2$ requires N, 18·67%). This compound easily undergoes decomposition when an alkaline solution is allowed to stand for sometime.

2-*Hydroxy*-4-*methyl*-5-*acetsulphanilamidothiazole* (*III*).—2- Hydroxy - 4 - methyl-5-aminothiazole (2 g.) in pyridine (5 c.c.) and acetone (10 c.c.) was treated with acetsulphanilylchloride (4 g.) under cooling. The mixture was carefully warmed at 50° C. for 15 minutes and then allowed to stand for 2 hours. On dilution with water (50 c.c.), a pinkish solid separated which was filtered, washed with water (yield, 2 g.) and crystallised from a mixture of pyridine and alcohol when it has m.p. 206° (dec.) (Found: N, 13·37. $C_{12}H_{13}N_3O_4S_2$ requires N, 12·84%).

2:4-*Dimethyl-5-acetsulphanilamidothiazole* (*IV*, *R* = *Ac*).—Crude 2:4-dimethyl-5-aminothiazole (5·3 g.) in dry pyridine (12 c.c.) was treated with acetsulphanilylchloride (11·8 g.). The reaction mixture was allowed to stay at the room temperature for 2 to 3 hours and then diluted with ice water. The crude product obtained (6 g.) was purified by dissolving in alkali (charcoal) and precipitating with acetic acid. On crystallisation from alcohol it separated in thick plates and had m.p. 220° (Found: N, 12·75. $C_{13}H_{15}O_3N_3S_2$ requires N, 12·92%). Jensen and Hansen[8] report m.p. 175° for this compound. This compound is soluble in dilute hydrochloric acid in contrast to the 2-acetsulphanilamidothiazole derivatives which are insoluble in dilute acids.

2:4-*Dimethyl-5-sulphanilamidothiazole* (*IV*, *R* = *H*).—The above described crude acetyl derivative (6 g.) was hydrolysed with dilute hydrochloric acid (60 c.c. of 4·5 N) under the usual conditions. This yielded the deacetylated product (4·3 g.) which on crystallisation from dilute alcohol or boiling water separated in thin plates and had m.p. 183° (Found: N, 14·68. $C_{11}H_{13}N_3O_2S_2$ requires N, 14·83%). Jensen and Hansen[8] give m.p. 183°.

2-*Methylthiazole*.—McLean and Muir[11] have stated that they could not prepare 2-methylthiazole from dichlorether and thioacetamide. We have, however, prepared it by this method though in bad yields.

A solution of thioacetamide (10 g.) in alcohol (20 c.c.) was treated with dichlorether (20 c.c.) in small quantities at a time under cooling (when the temperature was allowed to rise or the reaction product heated, the yield was further reduced). The reaction product was allowed to stand for 15 minutes, diluted with water (50 c.c.) and acidified with concentrated hydrochloric acid. The aqueous solution was decanted off from the pitchy product, extracted with ether, cooled, basified, the oil that separated taken up in ether and worked up as usual. The oil obtained of fractionation yielded 2-methylthiazole, b.p. 127–30° (yield, 2·7 g.).

2-β-(p-*Aminobenzenesulphonamido*)-*ethylthiazole* (*V*, *R* = *H*).—A mixture of 2-methylthiazole (2·7 g.) and finely powdered sulphanilamide (4·3 g.) in xylene (20 c·c.) was maintained at 120–125° and treated with paraformaldehyde (1·3 g.) in the course of 15 minutes. The reaction mixture was stirred well with a glass rod and the reaction was completed by heating for further 5 minutes. After decanting off the xylene the resulting hard mass was powdered and thoroughly extracted with ether and hot water. The compound was purified by dissolving it in alkali and precipitating with dilute acids (yield, 5·1 g.). It could not be crystallised from the usual organic solvents; m.p. 237–38° (Found: N, 14·66. $C_{11}H_{13}N_3O_3S_2$ requires N, 14·84%).

4-*Methyl-2-β-(*p*-aminobenzenesulphonamido)-ethylthiazole (V, R = Me)*.—This was prepared as the above described compound by treating a mixture of 2:4-dimethylthiazole (5 g.) and finely powdered sulphanilamide (7·6 g.) in xylene (35 c.c.) with *para*-formaldehyde (3 g.). The compound obtained (8·5 g.) could not be crystallised from the usual organic solvents but was purified by dissolving it in alkali and neutralising with acid; m.p. 241–42° (Found: N, 14·23. $C_{12}H_{15}O_2N_3S_2$ requires N, 14·14%.)

4-*Methyl-2-β-(*p*-acetaminobenzenesulphonamido) ethylthiazole*.— This compound was prepared as described above by using acetsulphanilamide in the place of sulphanilamide. It was purified by dissolving it in alkali and precipitating with acid; m.p. 211° (Found: N, 12·44. $C_{14}H_{17}O_3N_3S_2$ requires N, 12·39%). This compound caused no depression with that obtained by acetylating 4-methyl-2-(*p*-aminobenzenesulphonamido)-ethylthiazole with acetic anhydride.

2-*Hydroxy-4-methyl-5-(*p*-aminobenzenesulphonamido) methylthiazole (VI)*. An intimate mixture of 2-hydroxy-4-methylthiazole (2·3 g.), sulphanilamide (3·4 g.) and anhydrous zinc chloride (1·0 g.) was warmed at 50–60° with formalin (10 c.c.) for 2 hours. The thick sticky mass was cooled, powdered, washed with boiling water and dried. The compound (5·7 g.) was purified by dissolving in alkali and neutralising with acid. The amorphous white solid obtained turns yellow at 200°, then brownish and melted at 224–27° (Found: N, 13·77. $C_{11}H_{13}N_3O_3S_2$ requires N, 14·04%).

p-*Acetaminobenzene*-2-(4: 5-*dimethyl*)-*thiazolyl sulphone*.—(i) 2-Chloro-4:5-dimethylthiazole (3 g.) and potassium acetaminobenzene sulphinate (4·7 g.) in alcohol (15 c.c.) were refluxed for 4 hours. After removing the alcohol, the residue was diluted with water (20 c.c.) and the unreacted chlorothiazole extracted with ether. The crystalline white solid (0·25 g.) obtained was washed with water and dried. On recrystallisation from acetic acid it was obtained in rectangular plates and had m.p. 236° (Found: N, 9·12. $C_{13}H_{14}O_3N_2S_2$ requires N, 9·03%).

(ii) The chlorothiazole (3 g.) and the potassium salt (4·7 g.) were heated at 160–70° for 3 hours. The reaction mass, after washing with water and ether, was crystallised from boiling acetic acetic acid when it was obtained in glistening rectangular plates, m.p. 236° (yield, 3·5 g.). The ether washing gave back the unreacted chlorothiazole derivative,

(iii) The chloro compound (4·5 g.) and *p*-acetaminobenzene sulphinic acid (6 g.) in pyridine (20 c.c.) were heated for 4 hours. After dilution with water, the reaction product was filtered, washed free from pyridine with water and ether, and recrystallised from acetic acid (yield, 4 g.).

p-*Aminobenzene*-2-(4 : 5-*dimethylthiazolyl*) *sulphone*.—The above mentioned acetamino compound (3·0 g.) dissolved in glacial acetic acid (10 c.c.) was refluxed with dilute hydrochloric acid (5 c.c. of 1 : 1) for 90 minutes and the deacetylated product was precipitated by dilution. On crystallisation from an excess of boiling alcohol it separated in colourless plates and had m.p. 195° (Found: N, 10·23. $C_{11}H_{12}O_2N_2S_2$ requires N, 10·45%); yield, 2 g.

p-*Acetaminobenzene*-2-(5-*ethylthiazolyl*) *sulphone*.—2 - Chloro -5 - ethyl - thiazole (5 g.) and potassium *p*-acetaminobenzenesulphinate (7·1 g.) were heated at 170–80° for 4 hours. The fused mass was washed with water and then with ether. On crystallising the residue from 50% acetic acid, the sulphone melted at 172° (Found: N, 8·98. $C_{13}H_{14}O_3N_2S_2$ requires N, 9·03%); yield, 4·5 g.

p-*Aminobenzene*-2-(5-*ethylthiazolyl*) *sulphone*.—The above described acetyl compound (2 g.) was boiled with acetic acid (10 c.c.) and hydrochloric acid (10 c.c. of 1 : 1) for one hour. On diluting the resulting solution, the aminosulphone crystallised out. On recrystallisation from dilute alcohol, it was obtained in thick rhombic prisms and had m.p. 150° (Found: N, 10·31. $C_{11}H_{12}O_2N_2S_2$ requires N, 10·45); yield 1·4 g.

p-*Acetaminobenzene*-2-(5-*nitrothiazolyl*) *sulphone*.—To a solution of 2-bromo-5-nitrothiazole (10·5 g.) in boiling alcohol (75 c.c. of 50%) was added potassium acetaminobenzenesulphinate (13 g.). The condensation product separated out almost immediately as lemon yellow needles. The mixture was refluxed for 15 minutes more, the solid separated by filtration, washed with water and ether (yield, 15·6 g.). On recrystallising from glacial acetic acid, it had m.p. 200° (Found: N, 12·78. $C_{11}H_9O_5N_3S_2$ requires N, 12·84%).

p-*Aminobenzene*-2-(5-*nitrothiazolyl*) *sulphone*.—The above described acetyl compound (7·0 g.) in dilute acetic acid (50 c.c. of 1 : 1) was boiled under reflux with concentrated hydrochloric acid (7 c.c.) for 30 minutes. The deacetylated product separated as a deep yellow crystalline solid. The mixture was diluted with water and the amino compound collected after several hours. It was recrystallised from a mixture of dioxane and alcohol; the microcrystalline product obtained had m.p. 229° (Found: N, 7·72, $C_{15}H_{16}O_5N_2S_2$ requires N, 7·61%); yield, 3·6 g.

We thank Major-General Sir Sahib Singh Sokhey for his kind interest in these investigations and also the Lady Tata Memorial Trust for the award of a scholarship to one of us (A.V.).

SUMMARY

Condensation of 2-bromo-5-nitrothiazole with sulphanilamide yielded (i) in the presence of potassium carbonate and copper powder, 2-sulphaniamido-5-nitrothiazole and (ii) in alcoholic solution the isomeric N^4- (5-nitro-2-thiazolyl)-sulphanilamide. 2-Hydroxy-4-methyl-5-aminothiazole and 2:4-dimethyl-5-aminothiazole condensed with acetsulphanilylchloride to yield respectively 2-hydroxy-4-methyl-5-acetsulphanilamidothiazole and 2:4-dimethyl-5-acetsulphanilamidothiazole. The latter, on hydrolysis, furnished 2:4-dimethyl-5-sulphanilamidothiazole, which was about as active as sulphathiazole in experimental pneumococcal and *P. pestis* infections in mice but much more toxic. By condensing 2-methylthiazole, 2:4-dimethylthiazole and 2-hydroxy-4-methylthiazole with formalin and sulphanilamide, were obtained respectively 2-β-(*p*-aminobenzenesulphonamido) ethylthiazole, 4-methyl-2-β-(*p*-aminobenzenesulphonamido) ethylthiazole and 2-hydroxy-4-methyl-5- (*p*-aminobenzenesulphonamido) methylthiazole, none of which showed any therapeutic activity in experimental pneumococcal infections in mice. Condensation of potassium acetaminobenzenesulphinate with 2-chloro-4:5-dimethylthiazole, 2-chloro-5-ethylthiazole and 2-bromo-5-nitrothiazole, the corresponding 2-*p*-acetaminobenzene sulphonylthiazoles were obtained which were deacetylated to the corresponding amino compounds; these compounds also did not show any striking therapeutic activity.

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CHEMOTHERAPY OF MALARIA

Part I. A Study of the Methods of Synthesis of Diguanides

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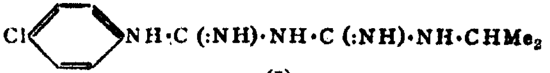
The present state of knowledge of the problem of malaria, and the targets of the chemotherapy of malaria have been discussed elsewhere.[1] The present communication forms a part of the work undertaken along those lines. Of the thousands of compounds studied in recent years, only the 8-aminoquinolines and N^1-*p*-chlorophenyl-N^5-*iso*propyldiguanide (paludrine, I) have been found to possess significant action on the exoerythrocytic form of *Plasmodium vivax* to be of any practical value. While the 8-aminoquinolines have little margin of safety, the action of paludrine is not intense enough. We have undertaken the synthesis of hybrids of these two structures to see if their properties could be reinforced in the same compound. In the synthesis of quinoline compounds with the substituted diguanide side chain, the problem initially turned out to be one of developing suitable methods for the construction of the required N^5-substituted side chain. So, we explored the various methods of synthesis of $N^1 : N^5$-disubstituted diguanides, taking paludrine (I) as the model compound. This paper presents some of the results obtained.



(I)

Paludrine consists of two guanidine units linked in series and so the methods of synthesis of the guanidines could be used for its synthesis by choosing appropriate reactants. The three standard methods that can be employed for the synthesis of the guanidines are as follows:

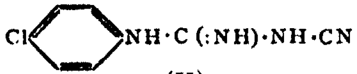
(i) $R \cdot NH \cdot CN + NH_2R' \rightarrow R \cdot NH \cdot C(:NH) \cdot NH \cdot R'$ (Erlenmeyer's synthesis[2])

$$\left.\begin{array}{l}\text{(ii)}\ R \cdot NH \cdot C(:NH) \cdot SMe + NH_2R' \xrightarrow{-HSMe} \\ \quad R \cdot NH \cdot C(:HR') \cdot SMe + NH_3 \xrightarrow{-HSMe}\end{array}\right\} \text{Rathke's synthesis}^{3,5}$$

$$\left.\begin{array}{l}\text{(iii)}\ R \cdot NH \cdot CS \cdot NH_2 + NH_2R' \xrightarrow{-H_2S} \\ \quad R \cdot NH \cdot CS \cdot NH \cdot R' + NH_3 \xrightarrow{-H_2S}\end{array}\right\} \quad 4$$

Many permutations and combinations are possible with these three methods and we have tried a number of them in which the reactants are easily accessible.

At the time the work was started, two methods of syntheses of paludrine had been published. The first one based on the work of Slotta and Tschesche[6] was worked out by Curd and Rose[7] and consisted of the condensation of *p*-chlorophenyldicyandiamide (II) with isopropylamine. This method has

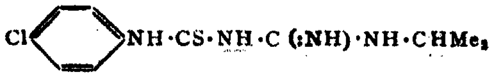


(II)

been studied in detail in this Institute and has been found to be the best and cheapest for the large-scale manufacture of this drug. We have found that N^1-*p*-chlorophenyl-N^5-*iso*propyldiguanide (I) on crystallisation from dilute alcohol separates in colorless needles which melt at 96–97°, solidify and then melt again at 125–6°. Only the latter melting point has been recorded by Curd and Rose[7] who crystallised this compound from toluene. The other method is due to Dasgupta and Basu[8] which consists in the condensation of *p*-chlorophenylguanidine with *iso*propylcyanamide.

Choosing as one reactant *iso*propylguanidine sulphate, which was easily prepared by the condensation of *iso*propylamine with S-methylthiourea sulphate, we tried three methods by condensing it with (1) *p*-chlorophenylcyanamide, (2) S-methyl *p*-chlorophenylisothiourea and (3) *p*-chlorophenylthiourea. In all these three cases the required N^1-*p*-chlorophenyl-N^5-isopropyldiguanide (I) was obtained, the maximum yield being obtained in the first case and the minimum in the last. In the case of the condensation with *p*-chlorophenylcyanamide, when *iso*propylguanidine sulphate was used in the place of the free guanidine derivative, a compound, m.p. 125–6°, but not identical with the required diguanide (I) was obtained in poor yields. When this work was completed, we came to know that patent applications have been filed by the Imperial Chemical Industries, Limited, covering substantially the same processes.

Attempts were next made to prepare the two compounds, N′-(*p*-chloroanilinothioformyl)-N″-*iso*propylguanidine (III) and N′-(*p*-chlorophenyl)-N″-(*iso*propylaminothioformyl) guanidine (IV), and then to replace the sulphur atom in them by the imino groups by known methods.[4, 5] But so



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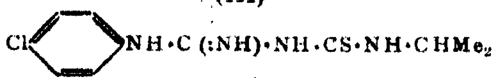
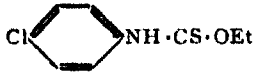


IX)

far, we have not succeeded in preparing either of these two compounds, though a number of methods were tried. Condensation of *p*-chlorophenylisothiocyanate with *iso*propylguanidine in alcoholic solution furnished a product, m.p. 104·5–5·5°, which was identified to be *p*-chlorophenylthiourethane (V). In benzene solution, no condensation product could be isolated. Similarly, phenylguanidine also did not condense with *iso*propylisothiocyanate. This confirms the conclusion of Slotta, Tschesche and Dressler[9] that the mustard oils condense with guanidine and *syn*diphenylguanidines but not with mono-substituted guanidines. The condensation of *p*-chlorophenylcyanamide with either thiourea or *iso*propylthiourea furnished only the polymerised products of *p*-chlorophenylcyanamide. *p*-Chlorophenylisothiocyanate condensed easily with isomethylthiourea to yield S-methyl-N-(*p*-chloroanilino) thioformylisothiourea (VI), m.p. 134·5–5° Attempts to replace the methylmercapto group in this compound by the amino or substituted amino groups led to unexpected changes. On boiling the compound with alcoholic ammonia, *p*-chlorophenylthiourea was obtained. By using *iso*propylamine in the place of ammonia under a variety of conditions, three products were isolated: (1) a compound, m.p. 125–6°, identified to be *p*-chlorophenyl*iso*propylthiourea (VII), (2) a compound, m.p. 157–8° which appears to be *p*-chlorophenylcyanthiourea (VIII) and (3) a compound, m.p. 203–5°, which has not been identified.



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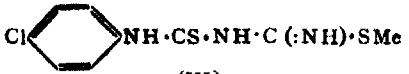

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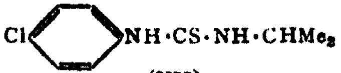

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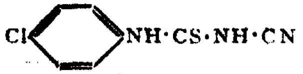
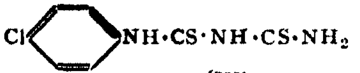


(VIII)

Attempts were then made to prepare compounds of type (III) through the phenyldithiobiuret derivative. On condensing two molecular equivalents of *p*-chloraniline with isopersulphocyanic acid, *p*-chlorophenyldithiobiuret (IX), m.p. 163–4°, was obtained. On boiling this compound with two molecular equivalents of mercuric oxide and ammonia, *p*-chlorophenyldicyandiamide (II) was obtained in good yields. This method is of particular interest because in the case of many amines, particularly the heterocyclic compounds not easy to diazotise, the dicyandiamide derivative could be prepared by this route. We have actually applied this to prepare quinoline derivatives and the results obtained will be published in due course. But in the attempts to prepare a compound replacing only the end thioamide group by the amidine group by using only one molecular equivalent of mercuric oxide and ammonia, the only crystalline compound isolated was the diacyandiamide derivative. On boiling *p*-chlorophenyldithiobiuret with two molecular equivalents of mercuric oxide and *iso*propylamine, N-*p*-chlorophenyl-N′-isopropyl-N″-cyanoguanidine (X), m.p. 151·5°, was obtained.



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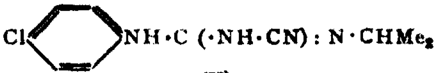
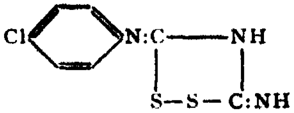


(X)

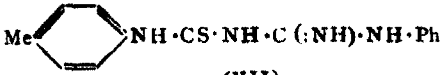
In this case also, using one molecular equivalent of mercuric oxide and *iso*propylamine, the anticipated compound (III) was not isolated. In *p*-chlorophenyldithiobiuret, the end thioamide group gets easily converted into the cyano group in the presence of desulphurising agents and it is not possible to replace the sulphur atom by the imino group. On the other hand, the sulphur atom in the thioamido group near the benzene ring undergoes this replacement quite easily. Thus, we have a good method of preparing compounds of formula (X) which we are utilising for the synthesis of many substituted diguanides by condensing them with the appropriate amines.

p-Chlorophenyldithiobiuret on oxidation with iodine in alcoholic solution yielded the hydroiodide of *p*-chlorophenylthiuret (XI). We could not crystalise the free base which is unstable.

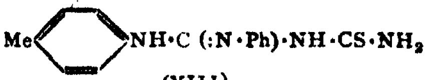


(XI)

On boiling this with alcoholic ammonia, a deep seated change took place and no crystalline product could be isolated. Fromm and Veller[10] have condensed *p*-methylphenylthiuret with aniline and *p*-toluidine and have isolated the two isomeric products (XII) and (XIII). We expected to obtain the compound (III) by boiling *p*-chlorophenylthiuret with *iso*propylamine.

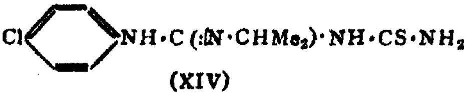


(XII)



(XIII)

Instead, the only compound isolated was found to be the isomer, N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine (XIV). The structure of this is confirmed since this compound on boiling with mercuric oxide in alcoholic solution furnished N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine (X).



(XIV)

On boiling the compound (XIV) with alcoholic ammonia and mercuric oxide, surprisingly enough, *p*-chlorophenyldicyandiamide (II) was obtained, the isopropylamino group being replaced by the imino group. The isopropyl group in the compound (X), however, is not replaced by boiling with alcoholic ammonia. Boiling *p*-chlorophenylthiuret with alcoholic ammonia and mercuric oxide yielded *p*-chlorophenyldicyandiamide, while by using *iso*propylamine in the place of ammonia, we obtained N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine (X).

Thus, in our work on the dithiobiuret and thiuret derivatives, though we did not succeed in preparing the compound (III), we have evolved a good method of preparing the dicyandiamide derivatives, which are particularly useful in preparing heterocyclic derivatives.

EXPERIMENTAL

Iso*propylguanidine sulphate.*—To S-methyl*iso*thiourea sulphate (30 g.) dissolved in the minimum amount of water, *iso*propylamine (20 c.c.) was added with shaking and the mixture refluxed cautiously for 3 hours and then vigorously for seven hours more, when the evolution of methylmercaptan almost ceased. The solution was evaporated to a syrup and lixiviated with alcohol, when *iso*propylguanidine sulphate separated from the mixture in a crystalline form (yield, 25 g.). It was collected and recrystallised from alcohol. The compound separated in needles and was very hygroscopic, m.p., 225–6°. (Found: N, 27·32; 27·4. $C_4H_{10}N$, 1/2 H_2SO_4 requires N, 28·1%.)

*N^1-*p*-Chlorophenyl-N^5-*iso*propyldiguanide* (*I*).—(i) The paper of Curd and Rose[7] does not contain exact details for the preparation of this compound and we have effected a number of improvements in this process which is being run on a pilot plant scale in this Institute.

To *p*-chlorophenyldicyandiamide (2 g.) in alcohol (40 c.c.) was added a solution of copper sulphate (1·6 g.) in water (6 c.c.) with good shaking so that the copper salt separated in a finely divided form. To this, *iso*propylamine (2 c.c.) was added and the mixture refluxed on the steam bath for four hours, when the green copper salt had turned completely pink. The alcohol was then evaporated off and the residue triturated with dilute hydrochloric acid (6 c.c. of con. acid diluted with 30 c.c. water), when practically all the copper salt went into solution. The filtered clear solution was treated with a concentrated solution of sodium sulphide, the copper sulphide filtered off, and the clear solution basified with a solution of sodium hydroxide when the diguanide derivative separated in a crystalline form (yield, 1·8 g.). On crystallisation from dilute alcohol, it separated in clusters of fine needles, m.p. 96–7° (solidifies and then melts again at 125–6°). This sample gave no depression in m.p. on admixture with a commercial sample similarly crystallised.

(ii) Sodium (0·3 g.) was dissolved in butyl alcohol (20 c.c.) and to this *iso*propylguanidine sulphate (3·8 g.) was added and shaken well. To the mixture, *p*-chlorophenylcyanamide (1·9 g.) was added and refluxed for 3 hours. The resulting mixture was diluted with ether (200 c.c.) and extracted with dilute hydrochloric acid (75 c.c. of 1 : 3). The acid extract after clarification with charcoal was basified with a solution of sodium hydroxide when the diguanide derivative separated as an oil and gradually solidified to a crystalline mass (yield, 1·5 g.). On crystallisation from dilute alcohol, it separated as a mass of fine crystalline needles, m.p., 96–97°, and was found to be identical with the product obtained in experiment (i). Alternatively, the butyl alcohol was steam distilled off and the resulting acid solution basified. But the product obtained by this proceedure was not as pure as that obtained by acid extraction.

(iii) Sodium (0·4 g.) was dissolved in butyl alcohol (50 c.c.) and to this *p*-chlorophenyl*iso*methylthiourea hydroiodide (3·4 g., prepared by the action of methyl iodide on *p*-chlorophenylthiourea) and *iso*propylguanidine sulphate (3·0 g.) were added, the mixture refluxed for 4 hours and worked up as above described, whereby 1·C g. of the diguanide derivative was obtained. In this experiment sodium bicarbonate was used in the place of sodium but the yield was considerably less than when sodium was used.

(iv) A mixture of *iso*propylguanidine sulphate (2·9 g.), *p*-chlorophenylthiourea (3·0 g.) and lead oxide (4·5 g.) in butyl alcohol (50 c.c.) was refluxed for six hours with good shaking. The mixture was filtered, the lead sulphide washed with butyl alcohol and the combined butanol solution worked up as indicated above, when about 0·25 g. of the diguanide derivative was obtained.

p-Chlorophenylthiourethane (*V*).—This compound was obtained by refluxing *p*-chlorophenyl*iso*thiocyanate for thirty minutes in alcoholic solution. It crystallised from dilute alcohol in beautiful needles and had m.p. 104–5·5°. (Found: N, 6·09; 6·20. $C_9H_{10}NSCl$ requires N, 6·49 per cent.). This compound was identical with that obtained when *p*-chlorophenyl*iso*thiocyanate was refluxed with *iso*propylguanidine in alcoholic solution.

S-Methyl-N-(p-*chloroanilino*)*-thioformylisothiourea* (*VI*).—To isomethylthiourea sulphate (4·9 g.) dissolved in water (20 c.c.) was added sodium bicarbonate (2·9 g.) followed by acetone (40 c.c.); to the solution *p*-chlorophenylisothiocyanate (4·8 g.) was added and the mixture refluxed for about two hours. The mixture which had separated into two layers was allowed to evaporate and the crystalline product that separated was collected (7·2 g.) and recrystallised from dilute alcohol. The condensation product was obtained in prismatic needles and had m.p. 134·5–135° (dec.). (Found: N, 16·05. $C_9H_{10}N_3S_2Cl$ requires N, 16·18 per cent.).

Action of alcoholic ammonia on S-methyl-N-(p-*chloroaniline*)*-thioformyl*iso*thiourea.*—S-Methyl-N-(*p*-chloroanilino)-thioformylisothiourea (1·0 g.) in alcoholic ammonia (50 c.c.) was gently refluxed for four hours and the solution evaporated to dryness. The residue on crystallisation from alcohol, yielded a product crystallising in thin needles, m.p. 175–76·5°. (Found: N, 14·9; 15·1. *p*-Chlorophenylthiourea, $C_7H_7N_2SCl$, requires N, 15·02 per cent.), which showed no depression in m.p. on admixture with a genuine sample of *p*-chlorophenylthiourea.

Action of iso*propylamine on S-methyl-N-*(p-*chloroanilino*)*-thioformyl*iso*thiourea.*—To S-methyl-N-(*p*-chloroanilino)-thioformylisothiourea (1 g.) in alcohol (20 c.c.) were added water (5 c.c.) and *iso*propylamine (2 c.c.); the mixture was refluxed for three hours, the solution evaporated to dryness and the residue crystallised from a mixture of benzene and little alcohol. A product crystallising in plates, m.p. 157–8°, (Found: N, 19·6; 20·1; 19·8 per cent.) was obtained, which appears to be *p*-chlorophenylcyanothiourea ($C_8H_6N_3SCl$ requires N, 19·85 per cent.).

In the above experiment, when a large excess of *iso*propylamine was used and the time of refluxing prolonged, two other products were obtained: (1) a compound crystallising in needles, m.p. 202·5–3° (Found: N, 16·75; 16·55; 16·8; 17·03 per cent.) and (2) a compound crystallising in fine needles, m.p. 124–5°, which was identified to be *p*-chlorophenyl*iso*propylthiourea by comparing it with a specimen prepared as indicated below.

*p-Chlorophenyl*iso*thiocyanate.*—This compound was prepared by Losanitch[11] by the action of iodine on bis-(*p*-chlorophenyl)-thiourea. The following method is a rapid one but the yield is only about 30 per cent. of the theoretical.

To *p*-chloroaniline (40 g.) suspended in alcohol (75 c.c.) and ammonium hydroxide (75 c.c.), was added carbon disulphide (45 c.c.) with good shaking. When the mixture warmed up, it was cooled in ice-bath. A clear solution was obtained and then the crystalline ammonium dithiocarbamate derivative separated. It was allowed to stand overnight, the crystalline product filtered, dissolved in water (about 1 litre) and a solution of lead nitrate (100 g.) added and the mixture subjected to steam distillation. *p*-Chlorophenyl*iso*thiocyanate passed over as an oil and solidified as a snow white crystalline mass; m.p. 46–7° (yield, 19 g.).

Iso*propyl*iso*thiocyanate.*—The preparation of this compound has been reported by Jahn[12]; the following method gives a better yield. *Iso*propylamine (84 c.c.) in water (150 c.c.) was cooled in an ice-bath and carbon disulphide (60 c.c.) was run in and shaken well. To this, under cooling, a solution of sodium hydroxide (40 g.) in water (230 c.c.) was added gradually in the course of about half an hour. A white precipitate separated. After allowing the mixture to stand for about two hours more, water was added to dissolve the crystalline solid, followed by a concentrated solution of mercuric chloride (136 g.). After shaking the mixture well, it was subjected to steam distillation. *Iso*propyl*iso*thiocyanate passed over as an oil; it was collected and fractionated; b.p. 138° (yield, 38 g.).

*N^1-Chlorophenyl-N^5-*iso*propylthiourea* (*VIII*).—This compound was obtained by refluxing (1) *p*-chlorophenyl*iso*thiocyanate with *iso*propylamine and (2) *p*-chloraniline with *iso*propyl*iso*thiocyanate, in alcoholic solution. On crystallisation from dilute alcohol it separated in beautiful needles, m.p. 124–5°. (Found: N, 12·17. $C_{10}H_{13}N_2SCl$ requires N, 12·26 per cent.)

p-Chlorophenyldithiobiuret (*IX*).—A mixture of *iso*persulphocyanic acid (3·0 g.) and *p*-chloraniline (5·1 g.) in alcohol (75 c.c.) was refluxed for two hours. The yellow *iso*persulphocyanic acid gradually disappeared and a crystalline product separated. The mixture was cooled, the solid obtained dissolved in cold 5 per cent. sodium hydroxide solution to free it from the accompanying sulphur, filtered and the clear filtrate acidified with concentrated hydrochloric acid whereby the condensation product separated as a bulky mass. It was separated by filtration (yield, 2·3 g.) and crystallised from dilute alcohol, whereby *p*-chlorophenyldithiobiuret separated in clusters of fine needles, m.p. 163–4°. (Found: N, 17·23; 17·41. $C_8H_8N_3S_2Cl$ requires N, 17·1 per cent.)

Action of alcoholic ammonia and mercuric oxide on p*-chlorophenyldithiobiuret.*—*p*-Chlorophenyldithiobiuret (2 g.) in alcoholic ammonia (50 c.c.) and mercuric oxide (3·8 g.) was refluxed on the steam-bath. The yellow oxide rapidly turned black. After refluxing for about four hours, it was filtered, the alcohol evaporated from the filtrate and the residue crystallised from dilute alcohol. The compound crystallising in thin leaflets, m.p. 202–3°, was identified to be *p*-chlorophenyldicyandiamide by comparing it with an authentic specimen.

In the above experiment, even when one molecular equivalent of mercuric oxide was used, the only product that could be isolated in crystalline form was the same *p*-chlorophenyldicyandiamide.

Action of iso*propylamine and mercuric oxide on p-chlorophenyldithiobiuret.*—*p*-Chlorophenyldithiobiuret (2 g.) in alcohol (50 c.c.) and *iso*propylamine (5 c.c.), was treated with mercuric oxide (3·8 g.) and the mixture refluxed on the steam-bath for four hours. The black precipitate was filtered off and the filtrate evaporated to dryness. On crystallisation from alcohol, a product separating in rectangular plates, m.p. 151·5°, (Found: N, 23·68 per cent.), was obtained which was identified to be N-*p*-chlorophenyl-N′-isopropyl-N″-cyanoguanidine (X) (see below).

p-*Chlorophenylthiuret (XI)-hydroiodide.*—*p*-Chlorophenyldithiobiuret (10 g.) in alcohol (100 c.c.) warmed to obtain a solution and to this a concentrated solution of iodine (10 g.) in alcohol was added till the decolorisation was complete and a faint colour of iodine was permanent. A bulky crystalline precipirate separated which rapidly became granular. This was cooled, filtered and washed with alcohol. The hydroiodide of *p*-chlorophenylthiuret thus obtained (10 g.) was used as such without any further purification.

Action of alcoholic ammonia and mercuric oxide on p-*chlorophenylthiuret.*—*p*-Chlorophenylthiuret hydroiodide (2 g.) in alcoholic ammonia (50 c.c.) was treated with mercuric oxide (1·8 g.) and the mixture gently refluxed for 3 hours. The black precipitate was filtered off, and the mother liquor, on working up as usual, furnished a product crystallising in thin plates, m.p. 202–3°, which showed no depression in m.p. on admixture with *p*-chlorophenyldicyandiamide.

Action of iso*propylamine and mercuric oxide on* p-*chlorophenylthiuret.*—In the above experiment when *iso*propylamine was used in the place of alcoholic ammonia, a compound, m.p. 150–1°, was obtained which was identified to be N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine.

N-(p-*Chlorophenyl*)*-N′-*iso*propyl-N″-aminothioformylguanidine (XIV).*—*p*-Chlorophenylthiuret hydroiodide (15 g.) suspended in alcohol (50 c.c.) was treated with *iso*propylamine (15 c.c.) and the mixture boiled for three hours. The alcohol was distilled off and the residue boiled with a small quantity of water and filtered hot to free it from the sulphur accompanying the product. From the filtrate, the condensation product crystallised out in fine plates (yield, 7 g.). On repeated crystallisation from water, it had m.p. 153–4·5°. (Found: N, 21·02; 21·12; 20·99; 21·19. $C_{11}H_{15}N_4SCl$ requires N, 20·70 per cent.)

p-*Chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine (X).*—The abovementioned compound (0·5 g.) dissolved in alcohol (20 c.c.) was treated with mercuric oxide (0·6 g.) and the mixture refluxed for about three hours. The black precipitate was filtered off and the residue on working up yielded the desulphurised product which crystallised from dilute alcohol in shining prisms and had m.p. 150–151·5°. (Found: N, 23·72; 23·94; 23·75. $C_{11}H_{13}N_4Cl$ requires N, 23·67 per cent.)

Action of alcoholic ammonia and mercuric oxide on the compound (XIV).—In this experiment, the compound that was isolated crystallised from alcohol and had m.p. 201–2° (Found: N 29·2. *p*-Chlorophenyldicyandiamide. $C_8H_7N_4Cl$. requires N, 28·6 per cent.) showing no depression in m.p. on admixture with a genuine sample of *p*-chlorophenyldicyandiamide.

Action of alcoholic iso*propylamine and mercuric oxide on the compound (XII).*—In this case, the compound isolated was identified to be N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine.

We are indebted to Mr. M. H. Shah of the Department who carried out the analyses recorded in this paper. We also thank Major-General Sir Sahib Singh Sokhey for his kind interest in these investigations.

SUMMARY

In the course of attempts to prepare quinoline derivatives with substituted diguanide side chains, the methods of syntheses of N^1-*p*-chlorophenyl-N^5-*iso*propyldiguanide (I) as a model compound have been investigated. The diguanide (I) was obtained by the condensation of *iso*propylguanidine with (1) *p*-chlorophenylcynamide, (2) S-methyl-*p*-chlorophenyl*iso*thiourea and (3) *p*-chlorophenylthiourea in the presence of lead acetate. Attempts to prepare the compound (III) by the condensation of *p*-chlorophenyl*iso*thiocyanate with *iso*propyl guanidine were unsuccessful. *p*-Chlorophenyl*iso*thiocyanate condensed with S-methyl *iso*thiourea to yield S-methyl-N^1-(*p*-chloroanilino)-thioformyl*iso*thiourea (VI but the methylmercapto group of this compound could not be replaced by either imino or *iso*propylimino groups. *p*-Chloraniline condensed with *iso*persulphocyanic acid to yield *p*-chlorophenyldithiobiuret which on boiling with ammonia and *iso*propylamine in the presence of mercuric oxide furnished respectively *p*-chlorophenyldicyandiamide and N-*p*-chlorphenyl-N′-*iso*propyl-N″-cyanoguanidine (X). *p*-Chlorophenyldithiobiuret on oxidation with iodine yielded *p*-chlorophenylthiuret which on treatment with ammonia and *iso*propylamine in the presence of mercuric oxide furnished respectively *p*-chlorophenyldicyandiamide and N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanguanidine. On treatment with *iso*propylamine, *p*-chlorophenylthiuret yielded only N-(*p*-chlorophenyl)-N′-*iso*propyl-N″-aminothioformylguanidine (XII), which easily undergoes desulphurisation to yield the compound (X); however, in the presence of alcoholic ammonia and mercuric oxide, *p*-chlorophenyldicyanamide was obtained.

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A NEW EFFECT OF HYDROGEN BOND FORMATION (CHELATION)

Part III. Isomerization of Rottlerone Analogous to Rottlerin-Iso-Allorottlerin (Isorottlerin) Change

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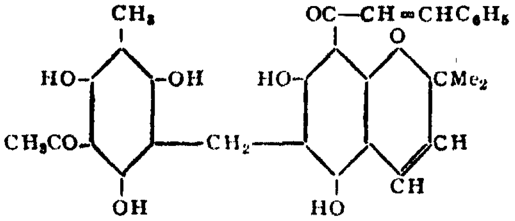
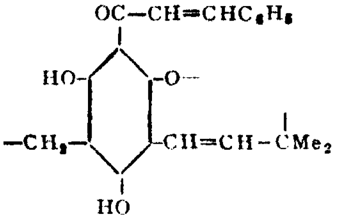
The isomerization of rottlerin into iso-allorottlerin (isorottlerin) was observed by a number of workers.[1,2,3]. Brockmann and Maier[1] considered it to consist of the cyclisation of the chalkone form into the flavanone. Mcgookin, Robertson and Tittensor[3] later showed that it was not a simple chalkone-flavanone change but involved further an interchange of the cinnamoyl and the substituted phloroglucinol residues. In their extremely careful and clear study of this interesting isomeric change, they expressed the opinion that it can best be explained on the view that the first stage of the reaction is the conversion of rottlerin (I) into the intermediate (II) by the opening of the chromene ring system and that this is followed by the reformation of the latter to produce (III) which is strictly analogous to rottlerin and termed allorottlerin. At the same time, the chalkone is cyclised to dihydro- r-pyrone system with the production of type (IV) which they regarded as representing Brockmann and Maier's isorottlerin and which they appropriately designated iso-allo-rottlerin. From the intermediate allorottlerin, two formulæ for the cyclisation product (IV and V) are possible but owing to lack of evidence a decision between the two orientations could not be made by them.

The most important and valuable point which the above authors have definitely made out is the shift of the chromene ring. The reason as to why this takes place has not so far been clear. Some light seems to be thrown on this question by the recent work of Narasimhachari and Seshadri[4] on a new effect of hydrogen bond formation. In their paper, the importance of a 5-hydroxyl for the stability of a flavanone structure has beeen brought out. It arises from the formation of a chelate ring involving the carbonyl group and the 5-hydroxyl. If there were no shift of the chromene ring and only the flavanone ring closure took place, a 7-hydroxyflavanone derivative (VI) would have resulted. But on account of the rearrangement of the chromene ring a 5-hydroxyflavanone derivative (IV or V) is obtained and this represents a more stable structure. The reason for the iso-allorottlerin change



(I)



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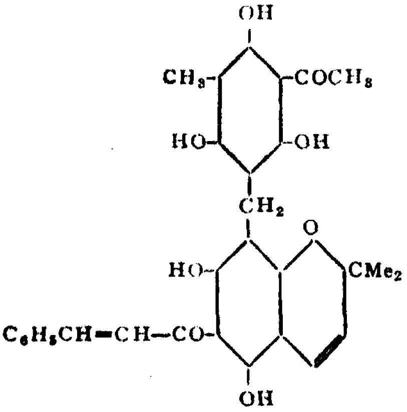

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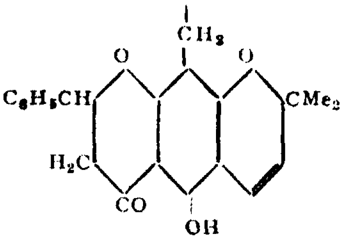

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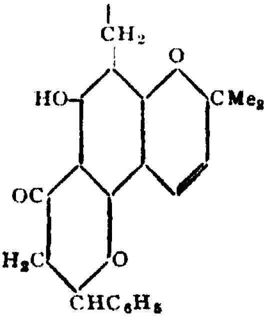
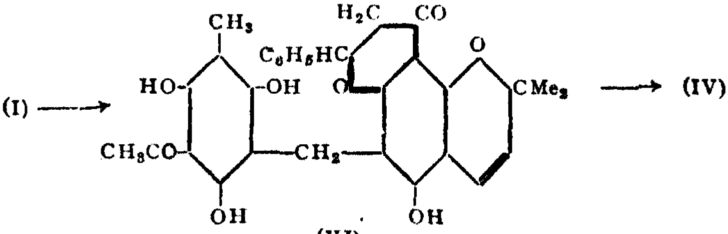


(V)

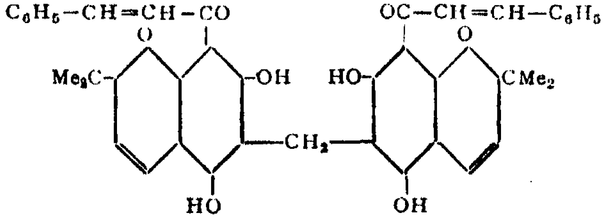
would therefore appear to be that thereby the molecule reaches greater stability.

Based on the above considerations it would be simplest to picture that the flavanone ring closure which generally proceeds readily in acid solutions, takes place first yielding the 7-hydroxy flavanone derivative (VI) and then the rearrangement of the chromene ring follows producing the stabler 5-hydroxy flavanone derivative. The constitution of isoallorottlerin then becomes reasonably certain as in (IV). But Robertson and his coworkers who recognised this possibility were not inclined to accept it because they felt that the closing of the dihydro-γ-pyrone ring involving the protection of a free hydroxyl group would tend to stabilise the chromene system and would thus hinder rearrangement. Some unequivocal evidence is therefore required to settle this point and it does not seem to be available at present. But at the same time it should be borne in mind that even in chalkones the ortho-hydroxyl is not entirely free and it is involved in a chelate ring.

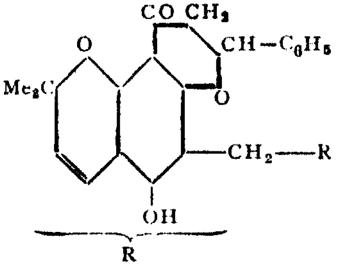


(VI)

No other example of this type of rearrangement seems to have been described in the literature. A closely analogous substance suitable for this study is rottlerone (VII), the main degradation product of rottlerin. Its constitution has been definitely established by Robertson and his co-workers[5] and it has all the structural features required for this test. In the past, Brockmann and Maier[1] reported that they did not get any definite reaction product by refluxing rottlerone with acetic acid. Mcgookin *et al.*[5] noticed that a yellow amorphous substance was formed under these conditions but stated that they had been so far unable to determine conditions required for cyclisation of rottlerone and the isolation of the resulting pure dihydro-γ-pyrone derivative. We have again examined this reaction. Rottlerone undergoes change almost completely by boiling its acetic acid solution for one hour. The deep red colour of rottlerone disappears and a pale yellow product is obtained in good yield. For it the name iso-allorottlerone is suggested. It could not be crystallised satisfactorily from any solvent, but could be obtained as an almost colourless (very pale yellow) crystalline powder from glacial acetic acid solution, by the addition of water. Though its melting point too is not very definite, it is clear that the isomeric change has taken place. The very pale yellow colour of iso-allorottlerone as contrasted with the highly coloured rottlerone is in agreement with the flavanone structure and the colour reaction with ferric chloride (immediate deep green colour) supports the presence of a hydroxyl group in the 5-position of each of the flavanone units. A hydroxyl in the 7-position does not give rise to any colour with ferric chloride. There is no possibility of attributing this ferric chloride colour to contamination with rottlerone because it gives an entirely different colour (brown). Iso-allorottlerone can therefore be considered to have a 5: 5′-dihydroxy-diflavanone structure (IX). The isomeric change taking place is very similar to the change of rottlerin into iso-allorottlerin, the possible intermediate 7-hydroxy flavanone stage being represented by (VIII).



(VII)



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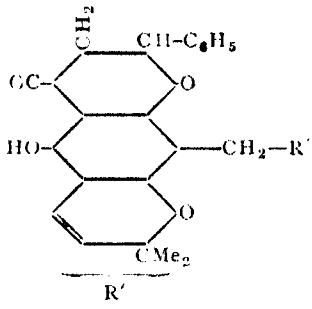

(IX)

Simpler and typical examples are further being investigated in order to test the validity of the above explanation of the isomeric changes.

EXPERIMENTAL

Rottlerone required for the following experiments was prepared from rottlerin using saturated barium hydroxide according to the method described by Mcgookin, Reed and Robertson.[6] It was obtained from chloroform-alcohol mixture in the form of garnet red prisms melting at 234–35°. It was very sparingly soluble in alcohol and insoluble in aqueous sodium carbonate solution. It was also insoluble in cold aqueous sodium hydroxide and on heating it decomposed forming a red coloured semi-solid, the solution turning yellow. With alcoholic ferric chloride, rottlerone gave first a very feeble brown colour which deepened on standing.

Iso-allorottlerone

Rottlerone (2 g.) and glacial acetic acid (50 c.c.) were heated on an oil-bath kept at 120–30° for one hour. By this time the initial bright red colour of the solution had completely changed to yellow. The solution was cooled and added to cold water and allowed to stand over night. The very pale yellow (almost colourless) substance that separated out was filtered and dried. Attempts to crystallize the product from acetone-alcohol, ethyl acetate-petroleum ether and ether-petroleum ether mixtures were not successful. But in the course of these treatments, particularly the last, some amount of sparingly soluble impurity could be removed. It was then taken up in glacial acetic acid, the solution treated with animal charcoal, filtered and diluted with water. This process was repeated several times. A very pale yellow (almost colourless) crystalline looking powder was thus obtained. It was insoluble in aqueous alkali even on heating and did not show any signs of decomposition. It gave an immediate deep green colour with alcoholic ferric chloride which was entirely different from the colour given by rottlerone. On heating it sintered at 98° and melted down to a liquid at 140°. (Found: C, 75·0; H, 5·8; $C_{41}H_{39}O_8$ requires C, 75·0; H, 5·8%.)

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FORMATION OF QUINONES BY OXIDATIVE DEALKYLATION

Part III. Alkali Fission of Gardenin

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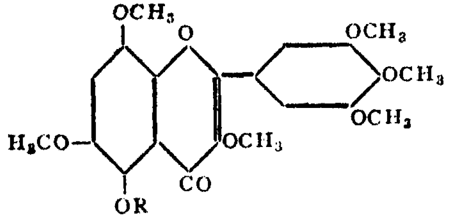
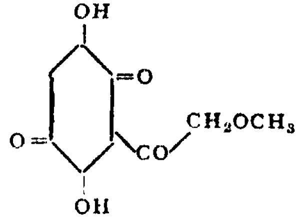
IN the study of the constitution of flavones alkali fission is an important operation. The use of aqueous alkali or aqueous alcoholic alkali gives the acid product representing the side-phenyl nucleus fairly readily. It is not, however, satisfactory for the isolation of the ketonic product representing the fused benzene ring. Absolute alcoholic potash is much more useful. Even here only completely methylated or ethylated flavones undergo fission satisfactorily whereas partial ethers having free hydroxyl groups are resistant. Bose and Nath[1] reported that when gardenin, 5-hydroxy-3 : 6 : 8 : 3′ : 4′ : 5′-hexamethoxy-flavone (I, R = H), was boiled with 15 per cent. alcoholic potash, they obtained trimethyl gallic acid and a chocolate-coloured compound melting at 158–60° having only one methoxyl group and exhibiting quinone and acid properties. Subsequently Bose[2] drew attention to the similarity between this compound and 2 : 5-dihydroxy-quinones in general and pedicinin in particular and concluded that it should have the structure (II). Employing gardenin methyl ether (I, R = CH_3) for the alkali fission, Balakrishna and Seshadri[3] showed that the fission went smoothly yielding a tetramethoxy-monohydroxy-ketone (III). By the action of nitric acid it underwent oxidative demethylation to form a neutral quinone-ketone (IV).



(I), R = H or CH_3



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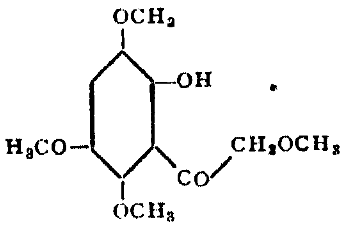

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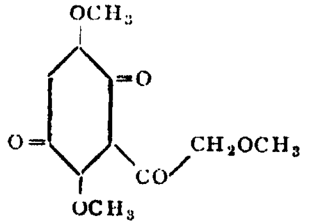

(IV)

It was felt necessary to study the observation of Bose and Nath in greater detail since it constituted a case of oxidative demethylation by means of alcoholic alkali, the intermediate stage being probably ω : 3 : 5-trimethoxy-2 : 6-dihydroxyacetophenone. Our present work confirms their observation. Further the constitution of the product is established as (II) by its preparation by the alkaline hydrolysis of the methoxy-quinone-ketone (IV). It should be noted here that all the nuclear methoxyl groups in ketone (III) can be removed through the stages (IV) and (II) because they are all in susceptible positions.[4] Further alkali is required for the demethylation of (IV) in conformity with the behaviour of 1 : 2 : 4 : 5-tetramethoxybenzene derivatives.[4]

Expecting that the above described behaviour of gardenin with alcoholic alkali may be characteristic of partial methyl ethers of flavones with a free hydroxyl group in the 5-position a select number of analogous compounds having some of the features of gardenin have been studied. They are tetramethyl-ether of quercetin, pentamethyl ethers of myricetin, quercetagetin and gossypetin having a free hydroxyl in the 5-position and calycopterin having free hydroxyls in the 5- and 4′-positions. Surprisingly none of these underwent decomposition with alcoholic alkali under conditions when gardenin gave a good yield of the dihydroxy-quinone-ketone (II). Only their sparingly soluble potassium salts separated out and remained unaffected.

EXPERIMENTAL

*ω-Methoxy-*3 : 6*-dihydroxy-*2 : 5*-quino-acetophenone* (*II*):

(i) *Hydrolysis of* ω : 3 : 6*-trimethoxy-*2 : 5*-quino-acetophenone* (*IV*).—The trimethoxy-quino-acetophenone[8] (0·8 g.) was just warmed with 40 per cent. aqueous potash (2 mols.) till a clear solution was obtained and cooled. The potassium salt separated out as a red solid. After allowing to stand for an hour it was filtered and washed with a small quantity of absolute alcohol. It was then dissolved in a few c.c. of water and the aqueous solution was acidified with dilute sulphuric acid. The brown solid that separated out, was extracted with ether and the ether solution concentrated. The product crystallised from alcohol as chocolate-coloured prisms melting at 159–60°. Yield, 0·3 g. (Found: C, 51·1; H, 4·0; OCH_3, 14·8; $C_9H_8O_6$ requires C, 50·9; H, 3·8 and OCH_3, 14·6%). An alcoholic solution of the substance, which was initially coloured orange, changed to dark brown on the addition of a drop of ferric chloride solution.

(ii) *Alkali fission of gardenin* (*I*, *R* = *H*).—Gardenin (2·0 g.) was treated with alcoholic potassium hydroxide (15%, 40 c.c.) and the mixture was refluxed for six hours. The solution was left overnight in the refrigerator. The brown potassium salt that separated out was filtered and washed with a little absolute alcohol. It was dissolved in a small volume of water and worked up as described in the previous experiment. The final product was identical in all respects with the compound obtained above and the mixed melting point was undepressed.

The fission could also be effected with 8% alcoholic potash; but then the reaction was not quite complete in 6 hours and required longer boiling for completion.

SUMMARY

The observation of Bose and Nath regarding the fission of gardenin with alcoholic potash is confirmed. The formation of ω-methoxy-3:6-dihydroxy-2:5-quino-acetophenone (II) in this reaction constitutes an example of oxidative demethylation by means of alcoholic potash. The same compound can be obtained from methyl gardenin through the stages (III) and (IV). Analogous partial methyl ethers of flavones with a free 5-hydroxyl are resistant to this treatment.

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